

Application No. \_\_\_\_\_

Exhibit No. \_\_\_\_\_

Date \_\_\_\_\_

Witness \_\_\_\_\_

BEFORE THE  
PUBLIC UTILITIES COMMISSION  
OF THE STATE OF CALIFORNIA

**GOLDEN STATE WATER COMPANY**

**PREPARED TESTIMONY OF  
ROBERT HANFORD AND  
MARK INSCO**

**Volume 9 of 10**

**ATTACHMENTS FH02 – P02**

Prepared by:  
GOLDEN STATE WATER COMPANY  
630 East Foothill Boulevard  
P. O. Box 9016  
San Dimas, CA 91773-9016

**July 2020**

**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT FH02**

**REGION 3**  
**FOOTHILL**



## ***ROHDE & ASSOCIATES LLC- EMERGENCY MANAGEMENT***

March 23, 2020

Dane Sinagra, P.E.  
Capital Program Manager  
Golden State Water Company

RE: Cowan Heights Wildfire Resiliency Review

Dear Dane,

Please find attached a summary of findings for the Cowan Heights District from our wildfire resiliency inspection conducted on March 5, 2020.

The System was found to be in relatively good condition with a mix of older buildings and upgraded sites. The Newport and Fairhaven sites are well within city boundaries, with no wildfire threat and are not included in this report.

<i>Facility Name</i>	<i>Status Summary</i>	<i>Wildfire Risk</i>
Clearview	Minor Recommendations	Low
Cowan Heights Warehouse	Moderate Recommendations	High
Fox Run	Moderate Recommendations	Moderate
Huntington Horn	Moderate Recommendations	Moderate
Kimberwicke	Minor Recommendations	Low
La Vereda	Minor Recommendations	Low
Peacock	Minor Recommendations	Low
Timberline	Moderate Recommendations	Moderate

Please let us know if you have any questions regarding this report. We anticipate your engineering staff may have additional questions regarding these findings. We will be happy to communicate with them directly as this occurs.

Sincerely,



Michael S. Rohde,  
CEO/Principal  
[MichaelSRohde@gmail.com](mailto:MichaelSRohde@gmail.com)  
(949)275-4545

[www.RohdeAssociates.net](http://www.RohdeAssociates.net)

***30 Via Gatillo, Rancho Santa Margarita, CA 92688 24 hrs.: 949.275.4545***

### **Clearview, Cowan Heights System**

1514 Clearview Ln, North Tustin

#### **Observations:**

This storage reservoir is in a historical fire corridor; however, it is located well within the community surrounded by private homes with irrigated and landscaped yards. The site consists of an above ground reservoir, booster station and partially sunken reservoir. All assets are constructed of non-combustible materials. The area is surrounded by a well-maintained gravel bed leading to perimeter fencing. There is ivy growing on the fence that is green with very little dead materials. Two plywood boxes are on the site to cover the booster stations; however they are not being used and are being stored near the fence line.

#### **Needs:**

Remove the plywood boxes from site. If the booster stations need to be covered recommend providing a cover made from non- combustible materials such as aluminum. Routinely inspect the perimeter fence line for signs of dead vegetation and remove if found. Continue with clearing annual accumulation of leaf litter and weed control.

#### **Additional Recommendations/Observations:**

None









**Cowan Heights Warehouse, Cowan Heights System**

10052 Brier Lane, Santa Ana

**Observations:**

The office and warehouse are located approximately 1/2-mile from Peter's Canyon Regional Park which includes 340 acres of coastal sage scrub, riparian, freshwater marsh and grassland habitats. The location is in direct alignment of a historical fire corridor and subject to strong Santa Ana winds. The general area experienced significant fire losses in the Green River Fire in 1948, consuming 22 homes, the Stewart Fire in 1958, consuming 16 homes, the Paseo Grande Fire in 1967, consuming 66 homes and the Santiago Fire in 2007 that consumed 15 homes.

Assets at this location include a 40-foot by 15-foot office building, a 45-foot by 39-foot warehouse both with plywood siding and 3-tab asphalt shingle roof and open eaves. The office building has open gable vents at each end that appear to not have screen protection. A trailered generator and other miscellaneous items are stored on the site, some directly against the buildings. The area is surrounded by asphalt and gravel and there is a green irrigated slope around the back side of the facility that consists of dead materials and overgrown mature trees.

Needs:

The buildings are showing signs of weather and wear with minor signs of dry rot damage at the ground level. Recommendation to replace any rotted wood, and maintain a fresh coat of paint to maintain wood integrity. Recommend enclosing the eaves on both buildings and ensuring the gable vents are fitted with 1/8-inch mesh materials to prevent ember intrusion into the attic space. Recommend additional maintenance on the surrounding slopes, removing dead materials and thinning the mature trees to provide separation horizontally and 10-feet vertically from the ground. For maximum protection, recommend replacing both buildings with ones constructed of fire resistive materials such as masonry or metal.

Additional Recommendations/Observations:

Maintain the area within the site free of ignitable materials such as annual leaf litter and relocate stored materials inside the warehouse or 15-feet from the building.

















**Fox Run, Cowan Heights System:**

9928 Fox Run Rd, North Tustin

**Observations:**

This site is shared with the local HOA who stores a large mulch pile to the rear of the property. The location is surrounded by tennis courts on one side and a private home on the others. There are mature eucalyptus and pine trees within irrigated maintained slopes. There is a 30-foot by 45-foot wood frame with stucco siding building that houses a booster station. The roof is Spanish clay tile with moderate pine needle litter build up. The eaves are open. There are two 3-foot by 3-foot vents with ¼-inch mesh. The area is within a historical fire corridor and although surrounded by improvements, is subject to ember ignitions from an approaching fire. There is a trailered generator parked on the site in close proximity to the slope.

**Needs:**

Routine maintenance is required at this site to remove build-up of leaf litter and pine needles. Recommend enclosing the open eaves and replacing the ¼-inch mesh on the vents with 1/8-inch mesh. Continue to maintain the slopes, removing dead materials and maintain tree trimming.

**Additional Recommendations/Observations:**

None









**Huntington Horn, Cowan Heights System:**

11272 Reservoir Rd, North Tustin

**Observations:**

This location is well within the community but because it is in a historical fire corridor it is subject to ember intrusion from a Santa Ana wind driven fire. The site is on top of a knoll, surrounded by mature pine trees and private homes. The reservoir is a concrete tank half buried and has a wooden roof with rolled roofing and open eaves with screened sides.

**Needs:**

Routine maintenance is needed at this site to remove leaf litter and pine needles from the roof and around the site. Recommend replacing the wooden roof with one made from fire resistive materials such as aluminum. As an alternative, recommend enclosing the eaves around the tank and replaced the screening with 1/8-inch mesh material.

**Additional Recommendations/Observations:**

This site is surrounded by mature pine trees that provide a level of view shedding for the site. Recommend annual tree trimming to remove dead branches and keep limbs no lower than 10-feet above the ground level.







**Kimberwicke, Cowan Heights System:**

1684 Kimberwicke Drive, North Tustin

**Observations:**

The booster pump is located in an underground vault in the street. An electrical/control cabinet sits on a concrete pedestal next to a sidewalk between private homes. There is a low risk of wildfire loss at this site; however, the location is within the ember fall zone for fires burning in this historic fire corridor and ornamental vegetation could be ignited in turn damaging the cabinet.

**Needs:**

Ornamental vegetation is planted around the cabinet to shield the view from neighbors. Recommend maintaining the vegetation 3-feet from the cabinet in all directions to reduce the risk of heat damage in the event of a fire.

**Additional Recommendations/Observations:**

None





**La Vereda, Cowan Heights System:**

11382 La Verdea, North Tustin

**Observations:**

This location is on the outskirts of the historical fire corridor and is surrounded by private homes. The assets within the site are protected by a masonry wall with the booster pumps located inside a concrete structure with a non-combustible roof. Exterior mounted equipment is mounted on a block wall covered by a metal roof. This site is at a low risk of impact from wildfire and is a good example of fire resistive best practice mitigations.

**Needs:**

There is a significant amount of ornamental vegetation in the neighbor that may produce leaf litter. Because this site is mostly enclosed it is subject to leaf litter build-up which may be ignitable if exposed to ember fall out. A fire of this type would be of low intensity and would likely not damage the facility. Recommend routine removal of accumulated leaf litter from the site.

**Additional Recommendations/Observations:**

None









**Peacock, Cowan Heights System:**

1131 Peacock Hill, North Tustin

**Observations:**

This location is on a hilltop with private homes below. There is a mix of native vegetation on the slope to the rear of the site with irrigated slopes throughout the remainder. The site consists of above ground and in ground reservoirs, generator, booster pump station and SCADA/electrical cabinets. There is a 30-foot by 50-foot vinyl fence around the booster pumps. The site is protected by chain link fencing. This is a well-maintained site covered with asphalt and gravel. Assets on the site are constructed of fire resistive materials and one in ground reservoir is currently being retrofitted with a metal roof. The location is within the historical fire corridor and is subject to ember fallout from fires burning in the Peter's Canyon Regional Park area. It is not likely to have ember ignited fires within the site; however, the site may be impacted by indirect heating from fires established on the surrounding slopes. The heat generated may be sufficient to result in damage or ignition of the vinyl fencing.

**Needs:**

The area within the fence lines are well maintained and require regular scheduled maintenance to maintain its pristine condition. The slope to the rear is overgrown with native vegetation and has been cleared to the property line. To provide maximum protection to the facility, recommend working with adjacent property owners to remove dead materials and reduce the fuel volume on the slope by 50% between the fence line and the homes below. While the risk is low, recommend to consider replacing the vinyl fence with one made from non-combustible materials such as aluminum.

Additional Recommendations/Observations:

This site is prone to storage and numerous pallets of both combustible and non-combustible items along with a debris pile were observed along the fence line. Recommend limiting the storage along the fence lines and allowing only non-combustible items to be stored in this location. Recommend removal of debris pile.

















**Timberline, Cowan Heights System:**

1008 Timberline Ln, North Tustin

**Observations:**

This location is on a hill top surrounded by native vegetation. The site is within a historical fire corridor and is in alignment for ember fallout from fires burning in the Peter's Canyon Regional Park area. There is a metal reservoir, 7-foot by 14-foot wooden shed with an open eave roof and electrical and SCADA equipment panels mounted on plywood sheeting and concrete pedestals near the perimeter fence line in close proximity to fuel beds. The area is free of ignitable materials with a well-maintained gravel bed surrounding assets.

**Needs:**

This site requires routine maintenance to remove leaf litter and control weeds within the fence line. The shed requires the eaves to be blocked in and enclosed. Recommend replacement of the wooden shed with one made from non-combustible materials such as masonry block. Recommend mounting the exposed cabinets on a non-combustible surface or relocating inside a fire resistive building.

**Additional Recommendations/Observations:**

It is likely that sufficient embers could fall into this site resulting in ignition of the wooden shed. It is likely that ember fallout will ignite native fuels on the slopes below and the site will be impacted by high indirect heat intensity. Recommend working with adjacent property owners to remove dead vegetation and reduce native fuels by 50% for a distance of 100-feet from the fence line to provide maximum protection to the site.











**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT FH03**

**REGION 3**  
**FOOTHILL**

***ROHDE & ASSOCIATES LLC-  
EMERGENCY MANAGEMENT***

March 20, 2020

Dane Sinagra, P.E.  
Capital Program Manager  
Golden State Water Company

RE: Claremont System Wildfire Resiliency Review

Dear Dane,

Please find attached a summary of findings for the Claremont System from our wildfire resiliency inspection conducted on March 4, 2020.

The Claremont System was found to be in upgraded condition with newer and well maintained equipment at most facilities. With the exception of the Claraboya Reservoir, the facilities are largely resilient to wildfire.

<i>Facility Name</i>	<i>Status Summary</i>	<i>Wildfire Risk</i>
Claraboya Reservoir	Moderate Recommendations	High
Lower O'Neil Reservoir	Minor Recommendations	Moderate
Upper O'Neil Reservoir	Minor Recommendations	Low
Fergus Falls Pressure Tank	Minor Recommendations	Low

Please let us know if you have any questions regarding this report. We anticipate your engineering staff may have additional questions regarding these findings. We will be happy to communicate with them directly as this occurs.

Thank you for your consideration,

Sincerely,



Michael S. Rohde,  
CEO/Principal  
[MichaelSRohde@gmail.com](mailto:MichaelSRohde@gmail.com)  
(949)275-4545

### **Claraboya Reservoir, Claremont System**

2733 N. Mountain, Claremont

#### **Observations:**

Good clearance within the site with gravel and asphalt surrounding the tank, generator and SCADA systems. Site is in a mid-slope location with a moderate fire risk. There is good fuel modification to the upper side of the site with natural and overgrown fuels to the down slope side of the site. The generator, electrical and SCADA cabinets are located on the edge of the down slope site exposing this equipment to the elements of fire from below. The site is accessed via a very narrow road that has vegetation on both sides, limiting access by fire equipment.

#### **Needs:**

This site would benefit from a fire resistive wall to deflect heat and embers from direct contact with the generator, electrical and SCADA system. Recommend a masonry wall 6 feet high x 140 feet long replace the chain link fencing between the generator and the down slope fuels.

As an alternative, native and non-native vegetation cover may be removed from the down slope side for a distance of 100-feet. However, it is reported that this is not part of GSW property and would require an agreement with the property owner. Additionally, fuel reduction maintenance would be required annually with an ongoing cost and potential disruption of view shielding for the plant.

#### **Additional Recommendations/Observations:**

Maintain the interior of the site free of combustible materials such as stored plywood sheets as well as accumulations of leaf litter. Trim trees that are encroaching into the site and ensure that annual fuel modification areas around the site are properly maintained. Reduce by 50 % and limb by 10 feet from the ground the heavier vegetation along the roadway 20 feet from the road surface on both sides.









### **Lower O'Neil Reservoir, Claremont System**

4726 Palmer Canyon

#### **Observations:**

This location is not currently being used. The site is subject to severe fire behavior with medium to heavy fuels on both slopes below.

#### **Needs:**

No current needs.

#### **Additional Recommendations/Observations:**

Should GSW reopen this site, recommend installation of a non-combustible roof structure and reduction of native fuels on the slopes by 50% for a distance of 100 feet.







**Upper O'Neil Reservoir, Claremont System:**

No address

**Observations:**

This is a new metal tank constructed below grade inside the remains of old concrete reservoir. The site is surrounded by a large gravel and asphalt area and while its location is prime for wildfire to burn through the facility has good resilience to wildfire. The concrete wall from the old tank serves as a fire resistive wall deflecting heat and embers from the main tank. Electrical

power is provided by a solar system mounted on the new tank, protected by the existing concrete walls.

Needs:

None

Additional Recommendations/Observations:

Maintain the site clear of annual leaf litter, continue with trimming of annual grasses along the exterior of the fence line.







**Fergus Falls Pressure Tank, Claremont System:**

1522 Fergus Falls, Claremont

**Observations:**

Located within a housing development and has good resilience to wildfire. The facility is surrounded by masonry walls with the interior covered by concrete slab.

**Needs:**

None

**Additional Recommendations/Observations:**

Remove any build-up of annual accumulation of leaf litter and trim tree branches that are encroaching into the site.







**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT FH04**

**REGION 3**  
**FOOTHILL**



***ROHDE & ASSOCIATES LLC-  
EMERGENCY MANAGEMENT***

March 23, 2020

Dane Sinagra, P.E.  
Capital Program Manager  
Golden State Water Company

RE: Morongo Del Norte Wildfire Resiliency Review

Dear Dane,

Please find attached a summary of findings for the Morongo Del Norte District from our wildfire resiliency inspection conducted on February 24, 2020.

The Morongo Del Norte was found to be in older condition with two sites under construction to upgrade equipment and add new facilities. All sites are surrounded by desert fuels and have a risk of impact from wildfire.

<i>Facility Name</i>	<i>Status Summary</i>	<i>Wildfire Risk</i>
Bella Vista	Moderate Recommendations	Moderate
Highway	Moderate Recommendations	Moderate
Navajo – Reservoir and Tank	Minor Recommendations	Low
Elm	Minor Recommendations	Low

Please let us know if you have any questions regarding this report. We anticipate your engineering staff may have additional questions regarding these findings. We will be happy to communicate with them directly as this occurs.

Thank you for your consideration,

Sincerely,



Michael S. Rohde,  
CEO/Principal  
[MichaelSRohde@gmail.com](mailto:MichaelSRohde@gmail.com)  
(949)275-4545

**[www.RohdeAssociates.net](http://www.RohdeAssociates.net)**

***30 Via Gatillo, Rancho Santa Margarita, CA 92688 24 hrs.: 949.275.4545***

### **Bella Vista, Morongo Del Norte System**

9345 Bella Vista Dr, Morongo Valley

#### **Observations:**

This facility is currently under construction adding a Uranium water treatment plant. The location is in desert landscape surrounded by desert sand and native vegetation. There is good clearance outside the perimeter fencing with the exception of the side where the electrical cabinets and shed are located. Electrical cabinets are mounted on metal pipes next to the perimeter fence and are exposed to flames and heat from an approaching fire. The shed is a 12-foot by 12-foot fiberglass shed with a fiberglass roof. The shed has one 12-inch by 12-inch vent with 1/4-inch mesh. There also is a generator on site. This area is subject to wind driven desert fires and is at risk of damage from wildfire.

#### **Needs:**

New construction should meet current Building Code Chapter 7-A standards for building in a wildfire area. If not replacing the fiberglass shed, the vent should be changed to one meeting current standards of 1/8-inch mesh. While costly, this site would benefit from a fire resistive wall around the entire perimeter to limit flames, embers and heat from impacting the equipment and buildings. Measurements were not taken of the perimeter due to construction. An alternative would be to reduce the surrounding vegetation by 50% for a distance of 100-feet around the site. This would require annual maintenance and annual costs. An additional option would be to provide fire resistive shielding around the electrical cabinets, generator and shed in the form of a fire resistive wall sufficient height to rise above each protected component. Walls should be placed between the equipment and the vegetation. Measurements were not taken due to construction and uncertainty of the final location of equipment on the site.

#### **Additional Recommendations/Observations:**

Maintain the interior of the site free of ignitable materials such as annual weeds or vegetation blown into the site.









### Highway, Morongo Del Norte System

9522 Sundown Trail, Morongo Valley (sign at the site indicates 9446 as address)

#### Observations:

Surrounded by desert landscaping, there is an 8-foot by 8-foot wooden shed with 3-tab asphalt shingle roofing and open eaves on this site. The shed has eight vents that are 12-inch by 12-inch with ¼-inch mesh. The area within the perimeter of the fence is desert sand and gravel with signs of annual weed growth. To one side of the site is a commercial stone sales business with a dirt road along the front and sparse desert vegetation surrounding the other two sides. The site is subject to the impacts of a wind driven fire which may result in loss of the wooden shed and damage to equipment.

#### Needs:

The wooden shed is the greatest asset at risk at this site. There are two options to protect the shed; enclose the open eaves and replace the eight vents with ones that meet current standards with 1/8-inch mesh or replace the entire shed with one made from fire resistive materials such as masonry block. For maximum protection, replace the perimeter chain link fencing with masonry wall 6-foot high by 240-feet in length.

#### Additional Recommendations/Observations:

Maintain the area within the perimeter free of annual grasses and other ignitable debris. Reduce fuels surrounding the site to maintain plant separation to limit the intensity of an approaching fire.





**Najavo, Morongo Del Norte System:**

8850 Navajo Trail, Morongo Valley (sign at site indicates address as 51620 Northridge Rd)

**Observations:**

There are two facilities at this site, a storage reservoir and a pump station with pressure tank. The storage reservoir is located mid slope surrounded by desert sand with sparsely populated light desert fuels. The reservoir has a low risk of damage from an approaching wildfire. The pump station and pressure tank is located at the bottom of the hill surrounded by desert sand and sparsely populated medium desert fuels. The risk at this location is also low, however it is at greater risk than the reservoir due to proximity of native fuels and construction features.



The pump station and pressure tank area has a generator on site along with electrical cabinets mounted on plywood 4-foot by 8-foot sheeting. Plywood boxes 4-foot by 8-foot by 2-foot cover the pumps.

Needs:

Reduce the fuels a distance of 50-feet surrounding the site to limit heat intensity of an approaching fire. For maximum protection, mount the electrical cabinets on a non-combustible surface. Recommend mounting to be similar to what is currently used to mount the cabinets containing the SCADA equipment. Recommend replacing the wooded covers with ones made from aluminum or other non-combustible materials.

Additional Recommendations/Observations:

Maintain the site clear of annual leaf litter, continue with trimming of annual grasses within the perimeter of the fence and around the exterior of the fence line of the pump station as well as the storage reservoir.









**Elm Street, Morongo Del Norte System:**

51318 Elm St, Morongo Valley

**Observations:**

The site is currently under construction adding a chlorine and uranium water treatment facility. The site is next to a dirt road adjacent to a single-family residence and open desert landscape. There is an 8-foot by 8-foot wooden shed with a 3-tab asphalt shingle roof, open eaves and with six 12-inch by 12-inch vents with ¼-inch mesh currently on the site along with electrical cabinets mounted on plywood sheeting against the rear fence line. The site is at low risk of impact from wildfire; however, construction features increase the risk of asset losses should fire burn through this area.

Needs:

The wooden shed is in average repair, showing signs of weather and wear. Recommend replacement of this shed with one constructed of fire resistive materials such as masonry block. At a minimum, the eaves should be enclosed and the shed should receive annual maintenance - caulking any cracks, applying fresh coat of paint and inspecting the roof. Additionally, the vents should be replaced with vents containing 1/8-inch mesh. The electrical cabinets should be mounted on a non-combustible surface or protected by installation of a fire resistive wall to separate the cabinets from adjacent fuel beds. Recommend installation of a masonry wall behind the cabinets, 10-feet in height and 12-feet in length.

Additional Recommendations/Observations:

Remove any build-up of annual accumulation of leaf litter and weed inside the perimeter fence and reduce the fuels for a distance of 50-feet surrounding the site.









**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT FH05**

**REGION 3**  
**FOOTHILL**

***ROHDE & ASSOCIATES LLC-  
EMERGENCY MANAGEMENT***

March 23, 2020

Dane Sinagra, P.E.  
Capital Program Manager  
Golden State Water Company

RE: San Dimas System Wildfire Resiliency Review

Dear Dane,

Please find attached a summary of findings for the Sam Dimas System from our wildfire resiliency inspection conducted on March 4, 2020.

The San Dimas System was found to be relatively good condition with newer and well-maintained equipment at two of the facilities. Both the Terrebonne Reservoir and the Eaglecliff Reservoir are at risk of impact from wildfire with recommendations made. While the Diversion Dam has a higher risk of wildfire, it is an abandoned site and poses no loss to GSW.

<i>Facility Name</i>	<i>Status Summary</i>	<i>Wildfire Risk</i>
Terrebonne Reservoir	Moderate Recommendations	Moderate
Eaglecliff Reservoir	Moderate Recommendations	Moderate
Diversion Dam	No Recommendations	Moderate

Please let us know if you have any questions regarding this report. We anticipate your engineering staff may have additional questions regarding these findings. We will be happy to communicate with them directly as this occurs.

Thank you for your consideration,

Sincerely,



Michael S. Rohde,  
CEO/Principal  
[MichaelSRohde@gmail.com](mailto:MichaelSRohde@gmail.com)  
(949)275-4545



**Terrebonne Reservoir, San Dimas System**

1532 North Terrebonne Ave

**Observations:**

This site is towards the top of a hill with steep canyons below. The location is aligned with factors which are conducive to severe fire behavior. Fire burning in the canyons below and driven by Santa Ana winds will most likely result in significant damage to the facility. Adjacent home owners have planted large trees to provide view screening, however these mature trees now contribute to the fire load increasing the risk to the facility. The tank is surrounded by gravel, however along the back side of the site the clearance between the tank and the fuels are only 15 feet. This limited distance may allow direct flame impingement on the tank potentially resulting in metal warping in areas above the water line causing catastrophic tank failure.

**Needs:**

This site would benefit from a fire resistive wall to deflect heat and embers from direct contact with the tank and components within the facility. Recommend a masonry wall 10 feet high x 300 feet long replace the chain link fencing that surrounds the site.

As an alternative, native and non-native vegetation cover may be removed from the down slopes for a distance of 200-feet. However, it is reported that this is not part of GSW property and would require an agreement with adjacent property owners. Additionally, fuel reduction maintenance would be required annually with an ongoing cost and potential disruption of view shielding for the plant.

**Additional Recommendations/Observations:**

Maintain the interior of the site free of annual weed growth and leaf litter. The site is surrounded by mature pine and eucalyptus trees along with native vegetation. Pine and eucalyptus trees are notorious for dropping needles and leaves, both which are easily ignitable. Trim trees within the property line and provide both horizontal and vertical separation if possible.











**Eaglecliff Reservoir, San Dimas System**

1947 Fernridge Drive

**Observations:**

Site includes a metal reservoir tank with external mounted electrical cabinets. Site is under construction, installing a fixed generator against the fence on the uphill side near the cut bank. This location will place the generator feet away from native vegetation and at risk of damage from fire. Half the site is protected by a well-maintained fuel reduction program, while the remainder of the site is surrounded by medium to heavy native vegetation including Sumac, Scrub Oak and Cactus. Electrical cabinets are mounted on the down slope side against the fence on plywood sheeting. Plywood housing covers ground piping near the tank and appears in serviceable condition. A fire burning from below will likely damage the electrical cabinets effecting the operations of this facility. Fire burning from above, if affected by winds may result in direct flame impingement on the tank resulting in blistering and potentially tank wall weakening.

Needs:

Continue with fuel reduction 100 feet around the entire site to alter fire behavior prior to reaching the site. Fuel modification will require annual maintenance at an annual cost and may require agreement with adjacent land owners. As an alternative, and for maximum protection, this site could benefit from replacing the chain link fencing with a fire resistive wall to deflect heat and embers from entering the facility. Recommend a masonry wall 8-foot high by 450 - foot length. At a minimum, the electrical cabinets should be relocated to inside a non-combustible building or protected by constructing a wall around three sides of the cabinets. This would require a wall 8-foot high by 16 feet.

Additional Recommendations/Observations:

The facility is surrounded by asphalt which provides good ground protection. Continue with removal of annual leaf litter and debris which easily ignites, in turn potentially igniting the plywood housings. Continue to maintain the plywood housings to prevent potential of embers lodging in cracks and causing ignition. For maximum protection, recommend replacing these units with non-combustible materials, such as aluminum.









**Diversion Dam, San Dimas System:**

No address

**Observations:**

The dam is abandoned and is in a creek along a paved road. The area is overgrown with native vegetation, however as this site is no longer used. While there is a moderate risk of wildfire in this area, there is no risk to GSW facilities.

**Needs:**

None

**Additional Recommendations/Observations:**

None





**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA01**

**REGION 3**  
**LOS ALAMITOS**



Sample Date	Site ID	sitelabel	Analyte	Result	Unit
1/11/2016	WO-BR-W	Ball Road Well	Manganese (total)	13	ug/L
2/2/2016	WO-BR-W	Ball Road Well	Manganese (total)	14	ug/L
2/9/2016	WO-BR-W	Ball Road Well	Manganese (total)	12.5	ug/L
3/1/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
4/4/2016	WO-BR-W	Ball Road Well	Manganese (total)	14	ug/L
5/2/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
6/6/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
7/5/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
8/1/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
9/6/2016	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
10/3/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
11/7/2016	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
12/5/2016	WO-BR-W	Ball Road Well	Manganese (total)	14	ug/L
1/17/2017	WO-BR-W	Ball Road Well	Manganese (total)	13	ug/L
2/13/2017	WO-BR-W	Ball Road Well	Manganese (total)	13	ug/L
3/8/2017	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
4/3/2017	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
5/1/2017	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
6/5/2017	WO-BR-W	Ball Road Well	Manganese (total)	17	ug/L
7/3/2017	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
2/5/2018	WO-BR-W	Ball Road Well	Manganese (total)	42	ug/L
2/8/2018	WO-BR-W	Ball Road Well	Manganese (total)	38	ug/L
2/12/2018	WO-BR-W	Ball Road Well	Manganese (total)	32	ug/L
2/23/2018	WO-BR-W	Ball Road Well	Manganese (total)	22	ug/L
3/5/2018	WO-BR-W	Ball Road Well	Manganese (total)	20	ug/L
4/2/2018	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
5/7/2018	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
6/4/2018	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
7/2/2018	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
8/6/2018	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
9/4/2018	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
10/1/2018	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
11/5/2018	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
12/10/2018	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
1/7/2019	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
2/4/2019	WO-BR-W	Ball Road Well	Manganese (total)	16	ug/L
3/4/2019	WO-BR-W	Ball Road Well	Manganese (total)	10.5	ug/L
3/4/2019	WO-BR-W	Ball Road Well	Manganese (total)	15	ug/L
4/25/2019	WO-BR-W	Ball Road Well	Manganese (total)	26	ug/L
5/6/2019	WO-BR-W	Ball Road Well	Manganese (total)	20	ug/L
6/10/2019	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
7/1/2019	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
8/5/2019	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
9/9/2019	WO-BR-W	Ball Road Well	Manganese (total)	19	ug/L
10/14/2019	WO-BR-W	Ball Road Well	Manganese (total)	17	ug/L

11/12/2019	WO-BR-W	Ball Road Well	Manganese (total)	18	ug/L
12/2/2019	WO-BR-W	Ball Road Well	Manganese (total)	25	ug/L
12/9/2019	WO-BR-T	Ball Road Well Plant Effluent	Manganese (total)	14.2	ug/L
<b>Average</b>				<b>21</b>	<b>ug/L</b>
<b>Max</b>				<b>42</b>	<b>ug/L</b>
<b>SMCL</b>				<b>50</b>	<b>ug/L</b>



**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA02**

**REGION 3**  
**LOS ALAMITOS**

## 2016 Complaint Summary

### 12. COMPLAINTS REPORTED (WRITTEN OR VERBAL)

Type of Complaint	No. of Complaints Reported by Customers	No. of Complaints Investigated	No. of Complaints reported to the Division of Drinking Water or Local County Staff	Brief Description of Cause and Corrective Action taken
Taste and Odor	0			
Color	74	74	74	Color water was caused by Bloomfield treatment plant backwash tank equipment failure. Corrective action included flushing customer line or main and conducting unidirectional flushing in the area.
Turbidity	0			

<http://drinc.ca.gov/EAR/PWSEarReport.aspx?printable=yes&SurveyID=17&PwsID=>

Visible Organisms	0			
Pressure (High or Low)	2	2	2	Investigated, specific to line or meter
Water Outages <sup>1</sup>	0			
Illnesses (Waterborne)				
Other (Specify)	3			Particulates, sand in water. Flushed customer line until clear.
Total No. of Complaints*	79	76	76	

<sup>1</sup>These are customer complaints of a water outage and not necessarily the same as the water outages reported under "System Pr  
Section of the EARDWP.

\*Calculated field

To update totals click here

**2017 Complaint Summary****11. COMPLAINTS REPORTED (WRITTEN OR VERBAL)**

Type of Complaint	No. of Complaints Reported by Customers	No. of Complaints Investigated	No. of Complaints reported to the Division of Drinking Water or Local County Staff	Brief Description of Cause and Corrective Action taken
Taste and Odor				
Color	23			
Turbidity				
Visible Organisms				
Pressure (High or Low)				
Water Outages <sup>1</sup>				
Illnesses (Waterborne)				
Other (Specify)	1			debris in water
Total No. of Complaints*	24	0	0	

<sup>1</sup>These are customer complaints of a water outage and not necessarily the same as the water outages reported under "System Problems" in the Distribution Section of the EARDWP.

\*Calculated field

To update totals click here

COMMENTS (Note: Comments will be made publicly available): ?

**2018 Complaint Summary****11. COMPLAINTS REPORTED (WRITTEN OR VERBAL)**

Type of Complaint	No. of Complaints Reported by Customers	No. of Complaints Investigated	No. of Complaints reported to the Division of Drinking Water or Local County Staff	Brief Description of Cause and Corrective Action taken
Taste and Odor				
Color	43	43		Construction related color complaints, undire
Turbidity				
Visible Organisms				
Pressure (High or Low)				
Water Outages <sup>1</sup>				
Illnesses (Waterborne)				
Other (Specify)				
Total No. of Complaints*	43	43	0	

<sup>1</sup>These are customer complaints of a water outage and not necessarily the same as the water outages reported under "System Problems" in the Distribution Section of the EARDWP.

\*Calculated field

To update totals click here

COMMENTS (Note: Comments will be made publicly available): ?



**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA03**

## **REGION 3 LOS ALAMITOS**

Sample Date	Site ID	sitelabel	Analyte	Result	Unit
4/18/2016 10:32:00 AM	WO-D14	9585 Mamota	Color	18	Color Units
5/2/2016 10:55:00 AM	WO-D14	9585 Mamota	Color	10	Color Units
11/21/2016 11:09:00 AM	WO-D14	9585 Mamota	Color	10	CU
12/20/2016 10:17:00 AM	WO-D14	9585 Mamota	Color	10	CU
6/18/2018 11:25:00 AM	WO-D14	9585 Mamota	Color	20	ACU
7/16/2018 11:23:00 AM	WO-D14	9585 Mamota	Color	5	ACU
9/17/2018 9:45:00 AM	WO-D14	9585 Mamota	Color	50	ACU
1/22/2019 10:06:00 AM	WO-D14	9585 Mamota	Color	20	ACU
4/15/2019 9:54:00 AM	WO-D14	9585 Mamota	Color	30	ACU
7/15/2019 10:29:00 AM	WO-D14	9585 Mamota	Color	30	ACU
7/18/2016 10:33:00 AM	WO-D15	10532 Hester	Color	2.5	CU
5/15/2017 10:20:00 AM	WO-D16	10152 St Alban St	Color	3	ACU

**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA04**

**REGION 3**  
**LOS ALAMITOS**



# Guidance for the Treatment of Manganese

Subject Area: Water Quality



# Guidance for the Treatment of Manganese



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The Foundation's mission is to advance the science of water to improve the quality of life. To achieve this mission, the Foundation sponsors studies on all aspects of drinking water, including resources, treatment, and distribution. Nearly 1,000 water utilities, consulting firms, and manufacturers in North America and abroad contribute subscription payments to support the Foundation's work. Additional funding comes from collaborative partnerships with other national and international organizations and the U.S. federal government, allowing for resources to be leveraged, expertise to be shared, and broad-based knowledge to be developed and disseminated.

From its headquarters in Denver, Colorado, the Foundation's staff directs and supports the efforts of more than 800 volunteers who serve on the Board of Trustees and various committees. These volunteers represent many facets of the water industry, and contribute their expertise to select and monitor research studies that benefit the entire drinking water community.

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# Guidance for the Treatment of Manganese

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## FOREWORD

The Water Research Foundation (Foundation) is a nonprofit corporation dedicated to the development and implementation of scientifically sound research designed to help drinking water utilities respond to regulatory requirements and address high-priority concerns. The Foundation's research agenda is developed through a process of consultation with Foundation subscribers and other drinking water professionals. The Foundation's Board of Trustees and other professional volunteers help prioritize and select research projects for funding based upon current and future industry needs, applicability and past work. The Foundation sponsors research projects through the Focus Area, Emerging Opportunities and Tailored Collaboration programs, as well as various joint research efforts with organizations such as the U.S. Environmental Protection Agency and the U.S. Bureau of Reclamation.

This publication is a result of a research project fully funded or funded in part by Foundation subscribers. The Foundation's subscription program provides a cost-effective and collaborative method for funding research in the public interest. The research investment that underpins this report will intrinsically increase in value as the findings are applied in communities throughout the world. Foundation research projects are managed closely from their inception to the final report by the staff and a large cadre of volunteers who willingly contribute their time and expertise. The Foundation provides planning, management and technical oversight and awards contracts to other institutions such as water utilities, universities and engineering firms to conduct the research.

A broad spectrum of water supply issues is addressed by the Foundation's research agenda, including resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide a reliable supply of safe and affordable drinking water to consumers. The true benefits of the Foundation's research are realized when the results are implemented at the utility level. The Foundation's staff and Board of Trustees are pleased to offer this publication as a contribution toward that end.

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Chair, Board of Trustees  
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Executive Director  
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## EXECUTIVE SUMMARY

Manganese (Mn) is a widespread water quality issue that impacts both surface and ground water utilities. Depending on the source of the Mn, the Mn concentration can vary seasonally or vary from source to source as the raw water supply strategy changes. Contamination of treatment chemicals by Mn or recycling flows within the plant can create variable levels of Mn as well. When Mn concentrations vary, the treatment challenges can be significant, depending on the treatment plant resources and the nature of the Mn occurrence. For utilities that have been unable to adequately meet Mn treatment challenges, the aftermath of colored water events can diminish consumer confidence in the water system and create direct costs to the entire community.

Water system operators and design engineers are expected to find practical, safe and affordable methods for removing Mn from drinking water. These solutions are often required to mesh with existing treatment facilities and water distribution systems without major improvements to the treatment processes or causing adverse impacts to other water treatment objectives like disinfection by-product (DBP) control.

The objective of this manual is to provide guidance to utilities and water professionals for the effective control of Mn through source water management and the design and operation of Mn treatment processes.





## CHAPTER 1 INTRODUCTION

### MANGANESE IN DRINKING WATER

Manganese (Mn) is one of the most abundant metals in the earth's crust, usually co-occurring with iron. It is a component of over 250 minerals but is not found naturally in its pure (elemental) form. Manganese typically occurs combined with other substances such as oxygen, silica, or carbonate. It is an essential nutrient for animals and plants: in humans and other animals it is important in both growth and nervous system functioning. For people, the typical daily intake for Mn is about 10 mg, the majority of which comes from natural occurrence in food sources.

Manganese is used principally in the manufacture of iron and steel alloys as well as an ingredient in numerous products. In the form of permanganate (Mn's highest oxidation state) it is used as an oxidant for cleaning, bleaching and disinfection. The United States does not produce Mn, so is reliant on imported Mn (USGS, 2007) and maintains stockpiles for emergencies. Manganese dioxide and other Mn compounds are used in products such as batteries, glass and fireworks. Other Mn compounds are used in fertilizers, varnish and fungicides and as livestock feeding supplements. More recently, an organic Mn compound has been used as an octane enhancer in unleaded gasoline in North America, Europe, Asia and South America.

Drinking water professionals have an interest in understanding Mn for a number of reasons. At relatively low concentrations (0.02 mg/L or greater), Mn can cause discolored water (usually black or dark red/brown), staining of laundry and plumbing fixtures and increased turbidity. At higher levels, Mn can create a metallic taste in water (0.1 mg/L or greater). These are concerns for both water customers and water utilities. Recent research work has documented the role of Mn in pipe scale formation and the impacts of later release of this store of Mn on water quality. Manganese can accelerate biological growth in distribution systems, with periodic sloughing of material that leads to black water problems.

### Current Manganese Regulatory Framework

Manganese is not currently regulated by the U.S. Environmental Protection Agency (EPA) as a primary drinking water standard. However, EPA has established a National Secondary Drinking Water Regulation for Mn that sets a non-mandatory water quality standard of 0.05 mg/L. This secondary maximum contaminant level (SMCL) is a guideline to assist public water systems in managing drinking water for aesthetic considerations, such as taste, color and odor. Manganese is identified by EPA as a contaminant that can cause both color problems and taste issues.

In 2004, the USEPA completed an evaluation of the need to develop a primary drinking water standard for Mn which concluded that, based on available data, regulation of Mn did not present a meaningful opportunity for health risk reduction. However, the USEPA has developed a Drinking Water Health Advisory document for Mn which reviews the existing health effects data. According to EPA, Mn is an essential nutrient at low doses, but chronic exposure to high doses may be harmful. Health effects from over-exposure to Mn are dependent on the route of

exposure, chemical form, age at exposure and an individual's nutritional status. The nervous system is the primary target organ in observed neurological effects. Reports of adverse effects from Mn exposure to humans are from inhalation exposure in occupational settings, with few data associating oral exposure to toxic effects.

The USEPA Mn Health Advisory recommends decreasing Mn concentrations to or below 0.050 mg/L, the SMCL for Mn, based on staining and taste considerations. A Lifetime Health Advisory Value (HAV) of 0.3 mg/L is recommended to protect against concerns of potential neurological effects. Lifetime health advisories are only developed for chemicals that are not likely to be carcinogenic to humans. The Lifetime HAV represents the portion of an individual's total exposure that is attributed to drinking water and is considered protective of noncarcinogenic adverse health effects over a lifetime exposure.

A few states have set 0.05 mg/L as an enforceable Mn standard for ground water and some have set enforceable standards for all supplies at levels ranging from 0.2 to 0.84 mg/L.

The Guidelines for Canadian Drinking Water Quality list an aesthetic objective level for Mn  $\leq 0.05$  mg/L.

World Health Organization (WHO) Guidelines for Drinking-water Quality set the health based level for Mn at 0.4 mg/L with the notation that concentrations at or below this level may affect the appearance, taste or odor of the water, leading to consumer complaints. WHO has also set an aesthetic guideline at 0.05 mg/L.

## **Manganese and Health Concerns**

Manganese is a necessary micronutrient for humans and has rarely caused toxic effects when ingested orally, probably because it is regulated in the body by homeostatic mechanisms (self-regulating through negative feedback). Poisoning by inhalation of high levels of Mn has been reported in industrial occupational settings. The Food and Nutrition Board of the National Academy of Sciences in 2001 defined an adequate intake level of Mn for adult men at 2.5 mg/day and for adult women at 1.8 mg/day. Manganese is found in nuts, grains, fruits, legumes, tea, leafy vegetables, infant formula and some meat and fish. The USEPA's Integrated Risk Information System (IRIS) includes a Mn Reference Dose for Chronic Oral Exposure (RfD) of 0.14 mg/kg-day, which translates to approximately 9.5 mg/day for a 150 lb person.

The neurological effects of inhaled manganese are well documented (USEPA, 2004), with "manganism" symptoms occurring, including weakness, anorexia, muscle pain, apathy, slow speech, monotonous tone of voice and slow clumsy movement of the limbs. By the oral route, Mn is often regarded as one of the least toxic elements. Some studies have reported neurological impairment as an effect of high doses of Mn, but the quantitative and qualitative details to establish direct causation are lacking. EPA summarizes these studies in the Mn Drinking Water Health Advisory document for those interested in more detail.

Much of the health effects research on Mn focuses on children because they may have more sensitive nervous systems and have less ability to self-regulate Mn in their bodies. A review of Mn metabolism in children and the exposure of infants to Mn (Ljung and Vahter, 2007) suggested that the WHO guideline should be revisited as it was based on adult exposure. Most recently, a study was published by Bouchard et al. (2011) that related Mn exposure and

children's Intelligence Quotient (IQ). Adjusting for confounding factors, the authors found that a 10-fold increase in Mn concentration at the tap was associated with a reduction of 2.4 IQ points. The median concentration of Mn in the households studied was 34 µg/L, a value below current aesthetic guidelines set by many regulatory agencies. As more research results become available, EPA may elect to revisit health assessments of Mn, with an eye toward developing a primary regulatory standard.

### **Recommended Treatment Goal for Mn**

While the regulatory secondary standard for Mn in drinking water is 0.05 mg/L, utilities should set a target Mn concentration in finished water of 0.015 mg/L. At 0.015 mg/L, issues of precipitation in the distribution system with later mobilization are minimized along with the chance for colored water events to occur.

### **MANUAL OBJECTIVE**

The objective of this manual is to provide guidance to utilities and water professionals for the effective control of Mn through source water management and the design and operation of Mn treatment processes. The control or management of Mn that has entered the distribution system is not addressed by this manual.





## CHAPTER 2

### SCIENCE OF MANGANESE

#### OVERVIEW OF THE SCIENCE OF MANGANESE

This chapter introduces basic aspects of the chemistry and biology of Mn and ends with some comments on the relationship between Mn and iron. Manganese, designated by the symbol Mn, is an element first isolated by Johan Gahn in 1774, although many of its properties have been known since antiquity. Mn is the twelfth most abundant element in the earth's crust and frequently is present in water supplies. Like most metals, the chemistry of Mn is complex and involves

- Oxidation/reduction reactions
- Precipitation/dissolution reactions
- Adsorption/desorption reactions

Adding to the complexity in understanding how Mn behaves in water systems is the fact that Mn can play an important role in microbiological processes. A firm understanding of Mn in drinking water systems requires an understanding of both the chemistry and the microbiology of Mn.

#### CHEMISTRY

Elemental Mn possesses an atomic number of 25 and atomic mass of 54.938 atomic mass units. It is located in the fourth period (row 4) of the periodic table in group seven (column 7). Chromium and iron are located immediately to left and right respectively of Mn on the periodic table. Iron (Fe) and Mn frequently occur at the same time in drinking water sources and there is a good deal of similarity in their chemistry.

Manganese is classified as a transition metal. A key characteristic of transition metals is that the electrons which participate in chemical reactions (valence electrons) are located in more than one shell surrounding the element's atomic nucleus. Hence, transition metals can exist in more than one valence or oxidation state. The presence of Mn in multiple oxidation states is an important feature of Mn chemistry, influencing both its occurrence and treatment.

#### Oxidation/Reduction

In theory, Mn exists in eleven oxidation states of which seven may be present in water (Table 2.1). As a practical matter, four oxidation states are the most important when considering drinking water treatment:

- Mn(II) oxidation state, typically the manganous ion,  $\text{Mn}^{2+}$ .
- Mn(III) oxidation state, typically a transitional state.
- Mn(IV) oxidation state, under ideal conditions  $\text{MnO}_2(\text{s})$ .
- Mn(VII) oxidation state, the permanganate ion,  $\text{MnO}_4^-$ .

**Table 2.1**  
**Manganese oxidation states in water**

Oxidation State	Compound	Name	Appearance
0	Mn	Elemental	Silvery solid
<b>II</b>	<b>Mn<sup>2+</sup></b>	<b>Manganous ion</b>	<b>Clear in water</b>
III	Mn <sup>3+</sup>	Manganic ion	Red/violet in water
	Mn <sub>2</sub> O <sub>3</sub> (s)	Manganese (III) oxide	Dark brown/black solid
<b>IV</b>	<b>MnO<sub>2</sub>(s)</b>	<b>Manganese dioxide</b>	<b>Black solid</b>
V	MnO <sub>4</sub> <sup>3-</sup>	Hypomanganate ion	Turquoise in water
VI	MnO <sub>4</sub> <sup>2-</sup>	Manganate ion	Green in water
<b>VII</b>	<b>MnO<sub>4</sub><sup>-</sup></b>	<b>Permanganate ion</b>	<b>Purple in water</b>

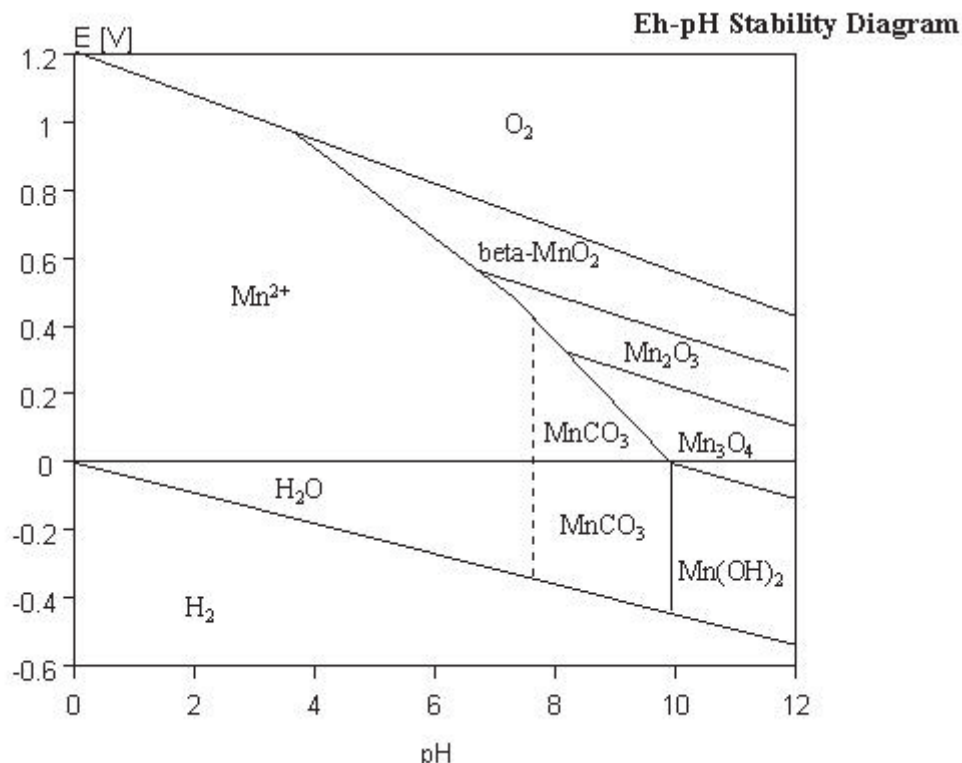
Important oxidation states for water treatment in **Bold**

The Mn(II) and Mn(IV) oxidation states naturally occur in water. Theoretically Mn(II) occurs as a soluble free metal divalent cation, Mn<sup>2+</sup>, while Mn(IV) occurs primarily as the insoluble oxide, MnO<sub>2</sub>(s). Particularly when background water chemistry has been changed by the addition of oxidants, other Mn oxide solids involving the Mn(III) or both the Mn(III) and Mn(IV) oxidation states may be present. For this reason Mn oxide solids are more accurately described collectively as MnO<sub>x</sub>(s), with x between 1.5 and 2. Hence for this manual Mn oxide solids are referred to as MnO<sub>x</sub>(s).

Permanganate, the Mn(VII) species, does not occur naturally in water but is an important manmade treatment chemical frequently used by water utilities. As implied by its high oxidation state (+VII), the permanganate ion (MnO<sub>4</sub><sup>-</sup>) is a strong oxidant capable of oxidizing many contaminants which are present in water. Permanganate is used for both taste and odor control and iron and Mn treatment. It is important to recognize that when permanganate acts as an oxidant in oxidation/reduction reactions, the soluble Mn(VII) is reduced to Mn(IV), creating additional Mn oxide solids.

Permanganate can be inadvertently formed in drinking water plants through excess oxidation of Mn(II) by strong oxidants such as ozone. See Chapter 6 for details.

The species of Mn which are present in water are controlled by the background oxidation/reduction potential and pH of the water along with the presence of other contaminants that can combine with Mn to form Mn compounds. The E<sub>H</sub>-pH (Pourbaix) diagram maps the Mn species that are theoretically stable over a range of background oxidation/reduction and pH conditions. In this diagram the y-axis represents the oxidation/reduction potential of the system, with oxidizing conditions present at the top of the diagram and reducing conditions present at the bottom of the diagram. The x-axis represents the pH of the system, with acidic conditions to the left and basic conditions to the right. This diagram supplies basic insight into how manipulation of oxidation/reduction potential and pH can be used to convert untreated Mn to Mn species that are suitable for treatment.



**Figure 2.1 Forms of Mn in water as a function of redox potential versus pH in presence of carbonate (Source: Scheffer F., and Schachtschabel P. 1989. Lehrbuch der Bodenkunde. Enke Verlag, Stuttgart.**

Figure 2.1 presents the stable forms of Mn in pure water containing Mn and carbonate. The manganous ( $\text{Mn}^{2+}$ ) ion is soluble and present over a wide range of oxidation/reduction and pH conditions. At pH levels typical of drinking water systems, (e.g., pH 6 to 8), soluble  $\text{Mn}^{2+}$  may or may not be stable depending on the oxidation/reduction state of the water and how much carbonate is present in the water. Under high pH or strongly oxidizing conditions  $\text{Mn}^{2+}$  is unstable and will precipitate to form a visible insoluble oxide, hydroxide or carbonate solid. Of course, the chemistry of drinking water systems is far more complex than described in Figure 2.1. However, this figure illustrates the key features of Mn chemistry with respect to drinking water treatment. In summary:

1. At low pH (<5) Mn is highly soluble.
2. At moderate pH (5 to 8) Mn is highly soluble under reducing conditions but insoluble under oxidizing conditions.
3. At high pH (>8) Mn is insoluble in the presence of significant amounts of carbonate. If pH is further increased, Mn forms various insoluble oxides.

One of the reasons why Mn so frequently causes problems for utilities is that typical drinking water quality conditions (pH, oxidation/reduction) are in the range in which Mn can readily cycle between soluble and insoluble forms. This explains in part why water colored by Mn can seem to appear and disappear in distribution systems.



## Precipitation/Dissolution

The formation of solids (precipitation) and the dissolving of solids (dissolution) are important features of drinking water Mn chemistry. Mn precipitation occurs when the water's ability to hold aqueous (dissolved in water) Mn is exceeded (e.g. the water is saturated with Mn). Mn precipitates out of solution and forms oxide, hydroxide or carbonate solids depending on the specific water quality conditions. Mn dissolution occurs when a Mn-containing solid comes in contact with water that is not saturated with Mn and has the ability to hold additional aqueous Mn. In this case, the Mn-bearing solid will dissolve. This process continues until water's ability to hold aqueous Mn is fulfilled or the solid is completely dissolved. A key feature for Mn is that the solubility of reduced Mn(II), or  $\text{Mn}^{2+}$ , is many orders of magnitude greater than the solubility of Mn(IV). Thus, reduction of oxidized Mn solids to Mn(II) results in dissolution and release of soluble Mn while oxidation of soluble Mn(II) to Mn(IV) results in precipitation of Mn solids. The solubility of important Mn solids and salts is presented in [Table 2.2](#).

**Table 2.2**  
**General solubility of important Mn solids and salts**

Solid/Salt	Mn Oxidation State	Representative Name	Comment
$\text{MnO}_2$	IV	Pyrolusite	Naturally formed solid – low solubility in water
$\text{Mn}_3\text{O}_4$	II/III	Hausmannite	
$\text{MnCO}_3$	II	Rhodochrosite	
$\text{KMnO}_4$	VII	Potassium permanganate	Treatment chemical – high solubility in water
$\text{NaMnO}_4$	VII	Sodium permanganate	

Equally important is the *rate* at which precipitation or dissolution occurs. Since some approaches for Mn treatment depend on the formation of insoluble Mn, it is desirable to manipulate oxidation/reduction and pH conditions in a way which favors quickly precipitating  $\text{MnO}_x(\text{s})$ . As discussed in Chapter 6, this entails adding a strong oxidant to the water at moderate or elevated pH conditions.

## Sorption/Desorption

Sorption, or adsorption, is a surface based phenomenon in which molecules in solution (solutes) are attracted to and then adhere to a surface. The extent of sorption is affected by many factors including the amount and type of solid surface and the affinity of a solute for the surface. The solute-surface interaction is controlled by several forces including specific chemical interactions, electrostatic charge and the degree to which a solute “prefers” the water phase (hydrophilic) compared to the solid phase (hydrophobic).

Cations and anions in water, including  $H^+$  and  $OH^-$ , are able to form surface complexes (i.e., become adsorbed) with solid metal oxides and hydroxides, such as  $MnO_x(s)$ . The strength of this interaction depends on the specific cations, anions and solid surface. As a result of surface complex formation, oxide surfaces have an electric charge that varies with pH (i.e., the concentrations of  $H^+$  and  $OH^-$ ) and the concentrations of other cations and anions. In general, cation sorption increases and surface charge becomes more negative, as pH increases, while anion sorption increases and surface charge becomes less negative (or more positive) as pH decreases. These effects of pH are significant for Mn oxide surfaces within the approximately 6 to 9 pH range experienced in drinking water treatment.

For Mn control, surface complex formation is very important for several reasons. One important aspect is that precipitated  $MnO_x(s)$  particles are typically negatively charged, which means they do not aggregate or deposit in media filters very well unless they are destabilized by coagulation. Another important aspect is that Mn oxide surfaces can form strong complexes with (e.g., adsorb)  $Mn^{2+}$  ions from solution and this interaction increases as pH increases. Fortunately, the adsorption of  $Mn^{2+}$  by Mn oxide surfaces greatly enhances the rate at which the adsorbed Mn(II) can be oxidized to Mn(IV); the so-called autocatalytic effect of Mn oxidation/precipitation. These two phenomena, sorption and surface oxidation, are the basis for the sorption/catalytic oxidation method of Mn removal described in Chapter 6.

## Interrelationship of Chemical Processes

The three chemical processes described above do not occur in isolation but are in operation all at once. Under conditions experienced in drinking water plants, oxidation/reduction and pH conditions control the oxidation state of Mn, usually Mn(II) or Mn(IV) (and perhaps Mn(III)). The oxidation state controls Mn solubility; Mn(II) will be present as soluble manganous ion, Mn(III/IV) will be present as solid  $MnO_x(s)$ . When deposited on a surface, Mn oxide in the form of  $MnO_x(s)$  provides significant surface area that has the capability to adsorb charged molecules, including the Mn(II) ion; the surface also catalyzes the oxidation of adsorbed Mn(II). When Mn oxides are present in the water column, the net negative surface charge of the  $MnO_x(s)$  can influence treatability, with the charged  $MnO_x(s)$  colloids being difficult to destabilize and coagulate. Both the degree of uptake of Mn(II) onto  $MnO_x(s)$  covered surfaces as well as the net surface charge of  $MnO_x(s)$  are affected by pH.

## BIOLOGY

Microbiological processes play a large role in controlling which Mn species are present in the environment. Microbiological processes facilitate and are largely responsible for the cycling of Mn between the dissolved Mn(II) state and the insoluble Mn(IV) state in soils, freshwater and marine environments. Hence these processes play a large role in determining how, when and where Mn is present in surface and ground water. In addition, through clever manipulation and control of microbiological processes, Mn(II) can be oxidized and removed by water treatment processes. Biological techniques for Mn treatment are discussed in Chapter 6.

### Manganese Oxidation

A number of Mn oxidizing organisms are present in nature. These include bacteria, yeasts and algae. These organisms can oxidize Mn via multiple pathways. The pathways can be classified as direct or indirect oxidation (Gounot, 1994).

Indirect oxidation occurs when Mn is oxidized as a consequence of biological activity. When indirect oxidation occurs, Mn does not directly participate in any biological activity or assist in providing energy to organisms. Instead, microorganisms create localized environmental conditions (such as changes in oxidation/reduction potential, or pH) or the formation of by-products which bring about Mn oxidation.

Direct oxidation occurs when Mn participates in reactions needed to support biological activity. In this case Mn(II) serves as an electron source for microorganisms. The exact mechanism by which Mn is oxidized varies from organism to organism. In a similar vein, the exact purpose for or outcome achieved by biological Mn oxidation is unclear and probably varies from organism to organism. Of the two Mn oxidation pathways, direct oxidation appears to be prevalent in the environment.

An important feature of biological Mn oxidation, independent of the specific pathway by which it occurs, is the tendency of oxidized Mn to form a crust of Mn oxides on the surface of Mn oxidizing bacteria. These Mn-coated bacteria form a particulate that can be removed from water by backwashing these bacteria from its support media or via traditional solid liquid separation processes.

### Manganese Reduction

Similar to the situation with Mn oxidation, a number of Mn reducing organisms are present in nature. These range from highly aerobic bacteria or fungi to strictly anaerobic bacteria. Overall, organisms that reduce Mn appear to be far more prevalent in the environment than microorganisms that oxidize Mn, although some bacteria are capable of performing both Mn oxidation and reduction. Similar to Mn oxidation, microorganisms facilitate Mn reduction via indirect or direct pathways.

Potential indirect pathways for Mn reduction include reduction caused by localized presence of reduced pH and redox conditions caused by bacterial metabolism. Inorganic by-products of bacterial metabolism such as sulfide produced by anaerobic sulfate reducing bacteria

can reduce Mn(IV) to dissolved Mn species. Organic by-products of bacterial metabolism are also capable of Mn reduction.

Direct reduction pathways primarily involve dissimilatory Mn(IV) reduction. In this process Mn reducing organisms directly use Mn(IV) for cellular respiration rather than oxygen. Replacing the role typically performed by oxygen in cellular respiration, Mn(IV) serves as a terminal electron acceptor. Mn(IV) accepts electrons produced by the oxidation of organic matter, while producing energy for the growth of the organism.

## RELATIONSHIP BETWEEN MANGANESE AND IRON CHEMISTRY

The objective of this manual is to assist water professionals in managing Mn in drinking water systems. This manual is not intended to address the management of Fe. Yet given the frequent co-occurrence of Fe with Mn in drinking water supplies and the fact that Fe can be present at much greater concentrations than Mn, it is important to understand how the presence of Fe in water supplies can influence the management of Mn.

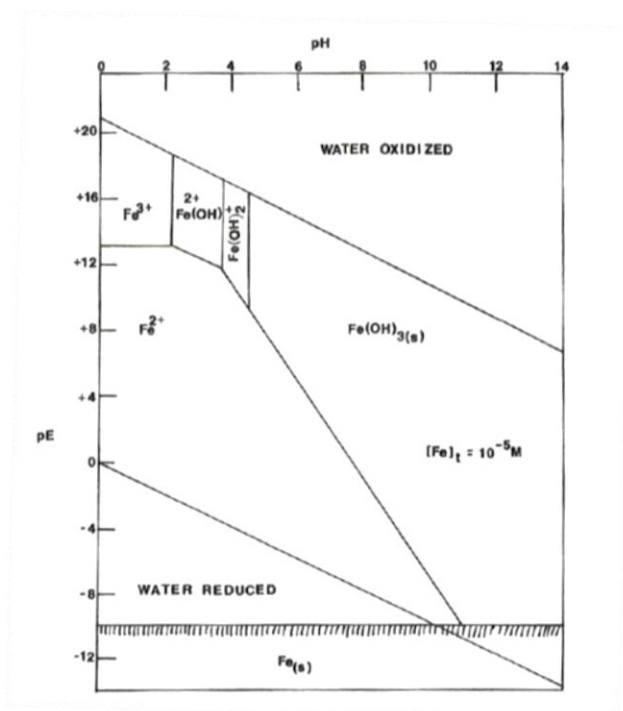
### Relevant Aspects of Fe Chemistry

Similar to Mn, the behavior of Fe in water is primarily controlled by oxidation/reduction potential and pH of the water in which Fe occurs. The combination of oxidation/reduction potential and pH has a strong influence on the species of iron present in the water. The species of iron present in the water in turn has a strong influence on its solubility.

In natural waters, Fe is generally present in two oxidation states, ferrous (Fe(II)) and ferric (Fe(III)). The Eh-pH diagram contained in [Figure 2.2](#) indicates which Fe species predominates under the combination of oxidation/reduction potential and pH conditions. Using this figure, some key features of Fe chemistry can be compared to the features of Mn chemistry presented in [Figure 2.1](#). In general:

1. At low pH (<5) unlike Mn, both Fe oxidation states are highly soluble.
2. At moderate pH (5-8) Fe tends to be more sensitive to changes in oxidation/reduction potential than is Mn.
3. At high pH (>8) both Fe and Mn tend to be insoluble.





**Figure 2.2 Forms of iron in water as a function of redox potential versus pH in pure water (Faust and Aly 1989)**

Another relevant aspect of Fe chemistry is that the transfer of only one electron is needed for Fe to move between the Fe(II) and Fe(III) state. In contrast, for Mn the transfer of two electrons is required to move between the Mn(II) and Mn(IV) state. Hence, on a molar basis twice as much oxidant is needed to convert dissolved Mn(II) to insoluble Mn(IV) than to convert dissolved Fe(II) to insoluble Fe(III).

### Impacts of the Presence of Fe on Mn Treatment

The differences in Fe and Mn chemistry are important when treating Mn in the presence of Fe. In general, Fe is far easier to oxidize than Mn at any pH. Also at moderate pH, Fe oxidation proceeds at a substantially faster rate than Mn oxidation. Hence the presence of dissolved Fe in water exerts an oxidant demand which must be satisfied prior to completing oxidation of dissolved Mn. Also at moderate pH typical of drinking water, Fe is readily oxidized in the presence of oxygen or chlorine while Mn is slowly oxidized by these compounds. For this reason aeration, which uses atmospheric oxygen to oxidize Fe, is quite effective for Fe oxidation but not for Mn oxidation. Similarly, prechlorination at moderate pH is effective for Fe oxidation, but is of limited effectiveness for Mn oxidation. Often utilities believe that Mn is being oxidized and precipitated with free chlorine when in fact Mn is being removed through the process of sorption and catalyzed surface oxidation on their filter media. Lastly, the presence of Fe also increases the overall dose of sequestering agents if they are used to stabilize Mn. All of these Mn control processes are discussed in detail in Chapter 6.

## **OTHER RECOMMENDED RESOURCES**

Manganese Chemistry: Pisarczyk K. 2005. Manganese compounds. Kirk-Othmer encyclopedia of chemical technology. Vol. 15.

Manganese Biology: Chapter 2 in, Kohl, Paul M. and Dixon, David. *Occurrence, Impacts and Removal of Manganese in Biofiltration Processes*. Water Research Foundation, 2012.



## CHAPTER 3

### SOURCES AND CAUSES OF VARIABLE MANGANESE

This chapter describes the various sources of Mn in water, both naturally occurring in source waters as well as may be found within treatment facilities. Causes of variability in Mn concentrations are also presented.

#### NATURAL MANGANESE IN GROUND WATER, SURFACE WATER AND RESERVOIRS

As one of the most abundant metals on earth, Mn comprises approximately 0.1 percent of the earth's crust. It is not found in pure elemental form, but is a component of over 100 minerals (ATSDR, 2008), including various sulfides, oxides, carbonates, silicates, phosphates and borates. There are approximately 250 known Mn minerals: pyrolusite (manganese dioxide), rhodocrosite (manganese carbonate) and rhodanate (manganese silicate) are some of the most common (Windholz et al., 1983). This section addresses the pathways by which naturally occurring Mn enters water.

#### Influence of Geochemistry and Biology on Manganese Occurrence

In the subsurface (soil, rock) Mn compounds are found as reduced dissolved or adsorbed Mn(II) and insoluble Mn(III) and Mn(IV) oxides. Movement of the insoluble forms of Mn into water is dependent on chemical conditions or microbial activity. Manganese can be dissolved as  $Mn^{2+}$  from solid oxide forms by reductive weathering and remains dissolved in this form as long as the solution is slightly acid and not too oxidizing. Precipitation of Mn(II) can occur when the pH increases, if carbonate or silicate are present in sufficient concentration.

If the solution becomes more oxidizing, as it will through prolonged exposure to air, Mn will precipitate as one of the oxide minerals. With adequate exposure to oxygen,  $MnO_2(s)$ , is the most stable Mn mineral at high oxidation/reduction potentials, but many other more complex minerals that include other cations can form. Rhodochrosite ( $MnCO_3(s)$ ) is stable over a wide range of potentials if dissolved carbonate is present in substantial concentrations. Manganese oxides commonly form first as colloids and may be transported long distances as colloidal suspensions. Because Mn colloids carry a negative charge over a large pH range, they preferentially adsorb naturally present cations from solution. Commonly found cations incorporated into Mn oxides include but are not limited to potassium, nickel, cobalt, lead, barium and copper. Precipitation of Mn oxides resulting from exposure to air can frequently be seen in natural deposits where they appear on surfaces or in cracks in rocks as black films (Krauskopf et al, 1995). In streams, naturally precipitated coatings of Mn oxide generally do not get very thick due to mechanical erosion, but in the bottoms of lakes or the ocean, deposits may be thicker. The rock on the left in [Figure 3.1](#) shows deposits of Mn oxide on its exterior because it is located in a stream near the outlet of a deep reservoir which has seasonal anoxic conditions at the depth of the outlet. A similar granite rock located near the same reservoir but not in the stream has biological growth on the upper surface but no Mn coating.





**Figure 3.1 Manganese oxide coating on granite rock on left below outlet from Cheyenne's Granite Reservoir and similar granite rock adjacent to reservoir without coating (Photo City of Cheyenne Staff)**

Manganese oxidation and reduction rates can be accelerated by bacteria. In fact, microorganisms are, either directly or indirectly, the major catalysts of Mn cycling in the natural environment. A variety of mechanisms and microorganisms are able to act in either oxidation or reduction of Mn at any solid/water interface, so the level of dissolved Mn in water is often variable.

Because Mn is an essential element in plant metabolism, it has been reported to accumulate in tree leaves, with some species of trees being more effective accumulators than others. Aquatic plants have also been noted to be accumulators of Mn. When plant materials die and are shed, they become available for dissolution in runoff and soil moisture. The importance of this source of Mn in river water is not well documented, but at least one study has demonstrated that it could be important in areas of the country where the volume of falling leaves is high at the same time that river flows are low (Hem, 1992).

## Ground Water

Dissolution of Mn oxides, carbonates and silicates is the natural source of Mn in ground water. In subsurface environments, the reduction of Mn(III) and Mn(IV) oxides into dissolved Mn(II) occurs in a complex chemical and biological environment. Microbes exist even at great depths in subsurface sediments, provided enough water, pore space and nutrients are available. Some pristine aquifers contain substantial oxygen and others may be anaerobic, depending on whether the aquifer is confined or unconfined and on the amount of organic material present. Depending on conditions in an aquifer, both oxidation and reduction of Mn can take place in the subsurface sediments via indirect and direct oxidation/reduction mechanisms (see Chapter 2). An extensive discussion of Mn oxidation and reduction in groundwater can be found in Gounot (1994).

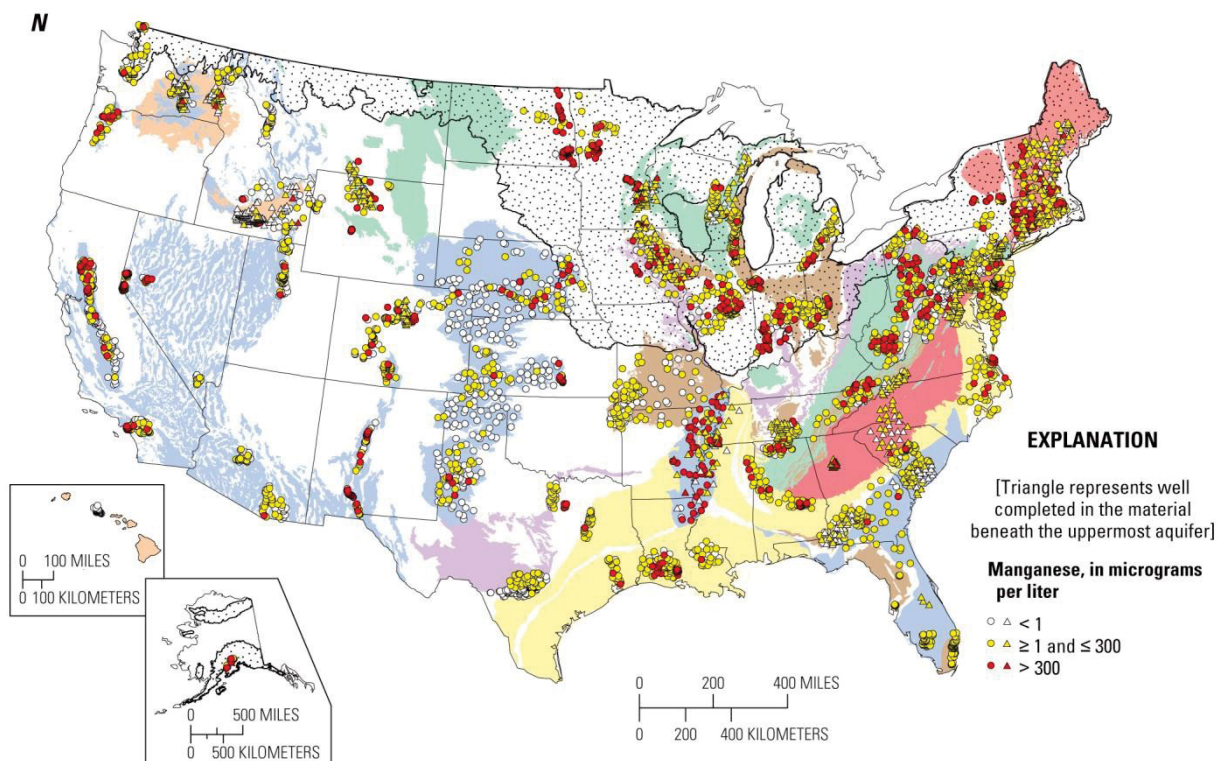
With respect to Mn concentration, a typical ground water well is likely to produce water with relatively consistent Mn concentration over time. However, ground water sources can vary significantly from one another, even among wells located in a single well field. Data from a

single well field in Nebraska are shown in [Table 3.1](#) to illustrate the range of Mn concentrations that can be found in a group of wells. In this example, all the wells are visible from a single location, so they are relatively close together. The differences between these wells are likely a result of the variability of Mn in the strata from which the wells are producing water. A ground water treatment plant drawing from these wells could experience highly variable Mn concentrations, depending on which wells were in service at a given time.

**Table 3.1**  
**Field data for well field “A” in Nebraska**

Well	Mn Concentration (µg/L)
1	430
2	10
3	0.2
4	<0.1
5	366
6	38
7	3.9
8	110
9	398

National occurrence data for Mn in groundwater was collected by the USGS as part of the national Water Quality Assessment Program between 1992 and 2003. The map in [Figure 3.2](#) was published by the USGS in 2011 as part of the compilation of this eleven-year survey of sources. This map does not identify all sources containing Mn because the sample set of wells was limited to those shown by the dots on the map. However, the variability of the concentration of Mn in wells is represented by the data included on the map. A large portion of wells sampled in this survey showed Mn > 300 µg/L. The data summary in the report indicates that of the 3,316 Mn samples obtained throughout the study, approximately 34 percent of them had Mn concentrations greater than 50 µg/L, the US EPA’s Mn SMCL. The colors on the map represent the areas covered by specific aquifers.



**Figure 3.2 Geographic distribution of Mn concentrations in groundwater collected from wells (USGS SIR 2011-5059).**

### Surface Water

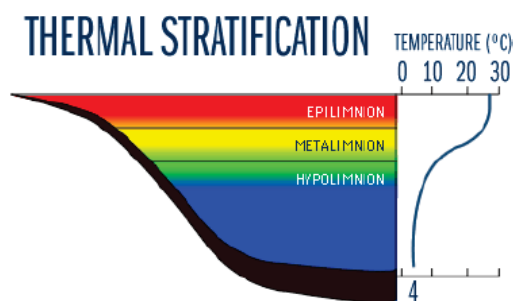
Manganese can occur in surface water supplies that come from both flowing streams and from storage lakes or reservoirs. Higher levels of Mn are often experienced seasonally in sources that are stored in reservoirs that become seasonally stratified. However, raw water supplies drawn directly from river or stream intakes can also experience variable Mn levels.

### *Lake/Reservoir Sources.*

Manganese compounds are typically present in the sediments residing on the bottom of the lakes or reservoirs. Since lakes and reservoirs are common features in source water collection systems, many surface water plants may need to deal with Mn at some time during the year. The basic problem utilities face is that dissolved Mn can be released from the sediment into the water column at concentrations which can ultimately result in colored water events for customers. The conditions leading to dissolved Mn released from sediments are a complex but predictable combination of physical processes that occur both on a reservoir wide basis and chemical/biological processes that occur at the sediment/water interface.

### ***Lake/Reservoir Wide Processes***

Most lakes and reservoirs exhibit the tendency to periodically thermally stratify into layers at certain points throughout the year. The warmer upper layer made up of less dense water is called the epilimnion. The colder and denser layer at the bottom of the lake or reservoir is called the hypolimnion. The metalimnion or thermocline is a transition zone between the epilimnion and hypolimnion. The thermocline is characterized by a large difference in temperature over a small increase in depth. The thermocline may be thought of as a barrier that separates the well mixed water of the epilimnion from the poorly mixed water of the hypolimnion. There is little movement of water across the thermocline, but solids and particulates in the epilimnion that are large enough to settle under the influence of gravity will cross the thermocline, moving from the epilimnion to the hypolimnion. The stratification layers in a lake or reservoir are shown in [Figure 3.3](#).



**Figure 3.3 Typical thermal stratification in a reservoir**

Thermal stratification develops when spring and summer solar heating warms surface water, causing a decrease in its density and a tendency for the warmed water to remain at the top of the lake. Water at the bottom of the lake, where sun light does not penetrate as readily, does not warm as rapidly as water at the surface. Hence the cooler and slower warming water tends to remain at the bottom of the lake due to its greater density. Wind provides energy to promote mixing of the lake and as long as the differences in water density are not too great, some mixing throughout the depth of the lake will occur. But eventually the wind can not provide enough mixing energy to overcome the differences in the density of the water and the lake stratifies. Once stratified, the lake may remain in this condition throughout the summer. In the late summer and fall, declining air temperatures cause the surface layers of the lake to cool. As the surface cools, the water eventually becomes denser than the underlying epilimnetic water. As the surface water sinks, additional mixing of the epilimnion takes place. Progressive mixing at greater depths from currents due to temperature shifts and from wind currents leads to lowering of the depth of the thermocline and thereby reducing the volume of the hypolimnion. Eventually, the entire volume of lake water mixes and fall *turnover* takes place. The final shift from weak stratification to complete mixing can occur within a few hours, especially if high winds are present. When turnover occurs, Mn, Fe and nutrients which have been trapped in the hypolimnion during stratification are rapidly released into the entire lake.



A different type of stratification process can occur when a lake/reservoir is covered with ice. In this case the coldest water, near 0° C, resides just beneath the ice layer. Slightly warmer, but denser water is found beneath the coldest water. This occurs because the temperature of maximum density of water is 4° C. This situation is sometimes called *reverse stratification* since the cooler water layer is above and not below the warmer water layer. Also, since ice cover prevents wind energy from mixing the lake, reverse stratification can occur even though the differences in water density are relatively small.

As temperatures warm in the spring, the ice cover on the lake/reservoir deteriorates slowly through ice erosion until the ice is saturated with water. The final loss of ice happens relatively quickly, leaving water at all depths with similar density and little resistance to mixing by spring winds. When the lake is mixed throughout the water column, spring turnover is complete and all the water is the same temperature.

In general, lakes and reservoirs in temperate zones experience both types of stratification. Lakes that mix twice a year are called dimictic lakes, experiencing turnover in both the spring and fall.

During summer stratification an important characteristic of the epilimnion is that the surface of the epilimnion is in contact with the atmosphere, allowing atmospheric oxygen to enter the water column and replenish oxygen in the water that has been consumed by biological activity, including bacterial respiration. Since the epilimnion is well mixed, primarily due to the input of energy from the wind, atmospheric oxygen is circulated throughout the epilimnion and is available to support biological processes. Dissolved oxygen (DO) is also generated within the epilimnion by photosynthesizing algae and is circulated by wind mixing as well. In contrast, the hypolimnion is isolated from atmospheric oxygen by the thermocline. As bacterial respiration proceeds in the hypolimnion, oxygen which cannot be replaced is depleted and the hypolimnion becomes anoxic.

Nutrients such as phosphorus enter the lake/reservoir via stream inflows. High levels of nutrients feed phytoplankton in the lake and a sequence of algae types in the epilimnion, creating a significant biomass that is a food source for microorganisms. As the algae die off at the surface of a reservoir, “rotting” algae fall through the water column to the bottom of the lake. When that algal mass reaches the hypolimnion, bacterial respiration continues to consume the dead algae, but the oxygen utilized is not replaced (i.e. no contact with the atmosphere and no algal-generated oxygen).

The degree and intensity to which the hypolimnion becomes anoxic depends greatly on the amount of nutrients entering the lake or reservoir. Oligotrophic lakes (lakes with very low biological productivity typically caused by a lack of nutrients) may have enough oxygen in the hypolimnion to remain oxic throughout the period of stratification. Eutrophic lakes on the other hand contain an excess of nutrients and are biologically very active. In the case of eutrophic lakes oxygen in the hypolimnion is consumed after stratification by biological activity, causing a prolonged and intense period of anoxia in the hypolimnion. Hence for anoxia and resulting dissolved Mn release from sediments to occur two conditions must be met. First, the lake/reservoir must stratify and second, sufficient biological activity must be present in the hypolimnion to consume oxygen that cannot be replaced from higher in the lake. The degree to which biological activity occurs is controlled largely by the nutrients, primarily phosphorous, which are available in the hypolimnion. An implication of this is that the effects of the depletion

of oxygen in the hypolimnion can be mitigated if oxygen in the hypolimnion consumed by bacterial respiration is artificially replaced. Also an overall reduction in the amount of nutrients entering the lake or reservoir may reduce the duration or intensity of an anoxic event.

### ***Sediment/Water Interface Processes***

Manganese compounds are typically found in the sediments of lakes or reservoirs. If dissolved Mn contained in sediments comes into contact with the water column at the sediment/water interface, the dissolved Mn in the sediments will diffuse into the water column, releasing Mn into the lake or reservoir. The depth at which dissolved Mn resides in sediments and the movement of dissolved Mn within sediments is controlled by how deeply oxygen from the water column diffuses into the sediments.

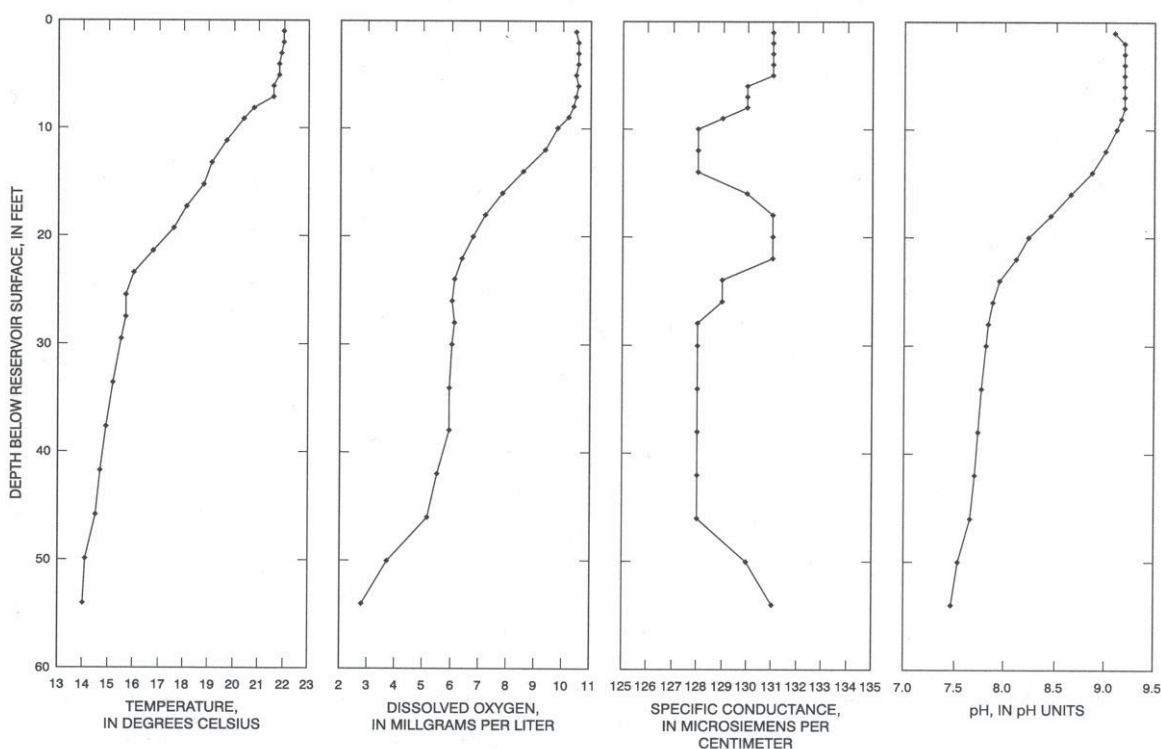
As long as oxygen can diffuse into the sediments, Mn is biologically cycled by microorganisms in the sediments. At depths in the sediments that oxygen cannot penetrate to by diffusion, biologically mediated Mn reduction continuously forms dissolved Mn. At the same time, in layers closer to the sediment/water interface in which oxygen is present, biologically mediated Mn oxidation continuously forms insoluble Mn oxidizing the reduced Mn that was generated by the Mn reducers deeper in the sediments. The reduced Mn moves upward in pore water through the sediments eventually coming into contact with Mn oxidizers, where the Mn is oxidized, precipitated and deposited in the sediment. In effect, the Mn oxidizers in the upper sediment layers stop the movement of dissolved Mn in the sediment by depositing precipitated Mn in the upper oxygen rich sediment layers. This process may be thought of as forming a 'cap' blocking the movement of dissolved Mn from the sediments into the water column.

When the concentration of oxygen in the water near the sediment/water interface decreases, typically after lake stratification, the Mn oxidizers migrate from the sediments into the water column looking for oxygen, removing the 'cap' which prevented dissolved Mn from being released into the water column. At this point dissolved Mn, previously trapped in the sediments, is released into the water column as Mn reducers move higher and higher in the sediments while processing the previously deposited Mn. Eventually the biological Mn reduction process moves completely out of the sediments and into the water column. At this point the Mn cycling process that previously operated in the sediments is recreated in the anoxic hypolimnion. At the top of the anoxic zone, where some DO is present, Mn oxidizing bacteria such as *Metallogenium sp* can utilize the dissolved Mn for energy and produce  $MnO_x(s)$ . After this solid is formed, it settles to the bottom of the lake where under more anoxic conditions it is acted on by the reducing bacteria and again Mn becomes dissolved, creating a Mn cycling process in the hypolimnion.

Once destratification occurs, oxygen is replenished in the water column above the sediment/water interface and the Mn cycling process moves back into the sediments, repeating the sequence described above.

### *Chemical Profiles of Stratified Lakes*

For a given reservoir, some general correlations can be developed between DO content and Mn release. For example, in Cheyenne's (WY) terminal reservoir, when DO is above 6 mg/L, algal growth is vigorous and little dissolved Mn is present. At DO content between 3 and 6 mg/L, some release of dissolved Mn into the water column is occurring. When DO is less than 3 mg/L, dissolved Mn is present and when DO is depleted, a significant amount of Mn is released from lake bottom sediments back into the water column increasing the concentration of Mn in the hypolimnion. Periods of the year when Mn will be elevated can be estimated from DO and temperature curves similar to those in Figure 3.4.



**Figure 3.4 Profiles for Crystal Lake Reservoir, Cheyenne, WY, for July 21, 1998 (USGS WRIR 99-4220)**

### *Implications for Utilities*

Water plants with intakes in the hypolimnetic zone of a stratified lake or reservoir will withdrawal water that is likely to contain elevated dissolved Mn concentrations during the summer and early fall. During the late winter another period of elevated dissolved Mn concentration is possible, but much less likely, since short days, ice cover and cold temperatures hinder biological activity which consumes oxygen in the lake or reservoir. Water plants with intakes in the epilimnion may experience brief periods of elevated Mn levels during turnover,

when the dissolved Mn released to the hypolimnion from sediments during stratification is dispersed throughout the lake or reservoir. This event may be accompanied by the release of Fe, ammonia, sulfites and other reduced compounds. In addition the release of nutrients from the hypolimnion into the entire lake/reservoir may stimulate algal blooms, particularly in the spring, causing taste and odor events.

An example of the variability of raw water Mn in a reservoir source can be found in the discussion of the Cheyenne case study in Chapter 7.

## **Stream Sources**

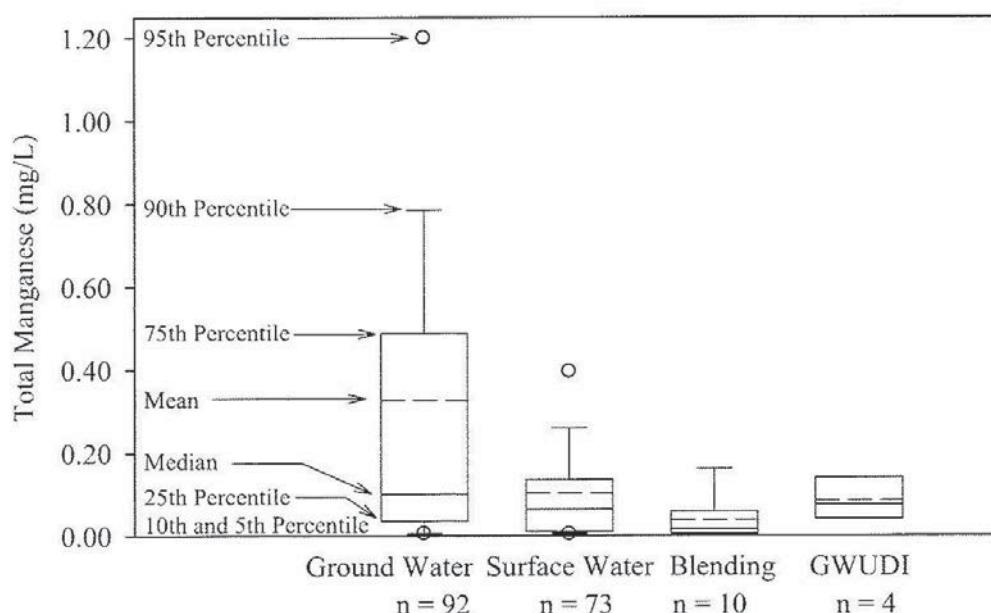
Manganese can and does occur in stream sources as a result of natural dissolution and erosion from the watershed. Particularly in areas where water supplies are impacted by runoff from mining, Mn can be both variable and elevated due to changes in stream flow. Data from areas of the country with coal mines or metal mines show that Mn can reach relatively high levels in surface runoff that reaches streams. Manganese levels as high as 10 mg/L have been reported in streams affected by drainage from coal mines (Hem, 1992). Dynamic variations in Mn have been observed in streams impacted by mine runoff that flow through wetland areas where biogeochemical processes alter the dissolved fraction of Mn (McKnight and Hrcir, 2000).

In areas where streams are not impacted by mine runoff, Mn variability can still be quite high, depending on the water sources feeding the stream and the stream flow conditions. Levels of Mn as high as 170 µg/L have been reported in streams in Missouri (Missouri Department of Natural Resources, 2007) that are fed from groundwater flows coming from areas where the groundwater is highly mineralized. In areas where groundwater does not play a role in stream flows, changes in source water during storm events can cause Mn variations. Streams flowing out of large reservoirs may have elevated Mn during summer months due to lake biological cycling processes. In general, the presence of oxygen in streams causes the slow oxidation and precipitation of Mn. This process serves as the ultimate control on dissolved Mn concentrations in streams. Evidence of oxidation and precipitation of Mn in streams can often be seen in the dark colored deposits of manganic oxides on the rocks in the stream bed (see [Figure 3.1](#)).

## **Comparison of Manganese in Ground Water and Surface Water Sources**

A survey of water systems relative to average source water Mn concentrations done by Kohl and Medlar (2006) illustrates the relative differences seen in Mn levels in ground water and surface water. The survey data are summarized in [Figure 3.5](#) and include responses from 172 systems. Based on this survey, the median levels of Mn in ground water and surface water are similar, but the mean level in ground water is approximately three times the mean level in the surface water sources that were reported in the survey. Thus, the variability of the average Mn concentration in overall ground water sources appears to be greater than observed collectively from surface water sources.





**Figure 3.5 Box-and-whiskers plot of average source water Mn concentration data from initial surveys, showing mean median and percentile ranges (Kohl, P. and S. Medlar, 2006)**

Because Figure 3.5 illustrates the range of values that utilities reported as average values, it does not reflect the maximum source water Mn concentrations that utilities have experienced. For practical purposes the major concern in designing and operating treatment plants is the maximum likely source water Mn concentration. This is because when water treatment is designed, the intent should be to be able to treat maximum Mn levels present in raw water entering the plant. So it is valuable to compare these average values with the maximums reported from the same survey as shown in Table 3.2. Although not enough information is available to make a direct comparison for specific utilities, the data indicates that wide variations in Mn concentrations are possible in both surface and groundwaters. Hence, when considering Mn treatment, utilities should collect sufficient water quality data to characterize the variability of raw water Mn concentrations. Information on sampling programs is included in Chapter 4.

**Table 3.2**  
**Maximum source water Mn concentrations reported in initial survey (Kohl,P. and S. Medlar, 2006)**

Source Water Type	Number of Utilities Responding	Maximum Mn Concentration (mg/L)
Ground Water	32	4.5
Surface Water	36	4.0
Blending of Ground and Surface Waters	6	2.0
Ground Water Under the Direct Influence of Surface Water (GWUDI)	3	2.3

## TREATMENT CHEMICAL CONTAMINATION

Water systems that utilize Fe coagulants have found that ferric sulfate and ferric chloride contain some Mn. The manufacturing process for ferric sulfate uses pickle liquor from steel manufacturing; likewise, ferric chloride is made using iron ore that is dissolved in hydrochloric acid. Both types of raw materials contain Mn that is carried over into the Fe solutions that are used for coagulants.

Fe-based coagulants can be manufactured with as little as 30 to 50 mg Mn/kg coagulant solution depending on the manufacturer. More typically, manufacturers produce coagulant solutions with Mn levels near 500 mg Mn/kg coagulant solution as the raw materials that are easily obtained for the manufacturing of coagulant solutions result in this level of Mn contamination in the finished product (Wodetzki, 2012). The form of Mn in Fe coagulants is dissolved  $Mn^{2+}$  due to the low pH of the solutions. In most treatment trains, the addition of dissolved Mn in the rapid mix is not desirable. This is because in plants where Mn is to be treated by oxidation followed by solid/liquid separation, the addition of an oxidant (frequently permanganate) typically (and should) precede the rapid mix. Hence, dissolved Mn added to the water by a coagulant solution during rapid mix process may not be adequately oxidized for removal later in the treatment train.

Material Safety Data Sheets (MSDS) for Fe coagulants typically do not report Mn content, so utilities that wish to know Mn content need to request the information from the supplier or measure it themselves in the delivered supply. To limit Mn in Fe-based coagulant supplies, utilities must provide specifications for bidding to the suppliers which limit the Mn content. In general, manufacturers indicate that specifying lower Mn levels in Fe-based coagulants means higher costs for the chemical.

Some utilities have initiated evaluations of the cost tradeoff between paying for lower Mn levels in coagulants and paying for additional oxidants or another treatment approach to remove the Mn contributed by the coagulant. For example, in Cheyenne (WY) the raw water Mn concentration has been reduced to near zero by aeration of the utility's terminal water reservoir. As a result the utility can justify paying higher costs to purchase Fe-based coagulants with low Mn content as it effectively removes the need to feed an oxidant into the raw water pipeline for

oxidation prior to rapid mixing and coagulation. The plant was able to directly compare the cost of feeding chlorine dioxide (the oxidation system in place) against the premium cost for low Mn in their Fe-based coagulant supply. In other plants, where variable raw water Mn levels are often present, the cost tradeoff might be a bit more complex to evaluate as it would require estimating the incremental increased cost to treat slightly elevated Mn. That cost might include additional oxidant addition, additional coagulant addition and perhaps an incremental increase in sludge solids management costs.

An example of a municipal specification that limits Mn content in a coagulant is provided in the Appendix A courtesy of the City of Cheyenne (WY) Board of Public Utilities.

## RECYCLE STREAMS

Treatment plants that remove naturally occurring Mn in treatment processes typically have waste streams that contain substantial levels of Mn. Waste streams generally consist of spent filter backwash water or sludge solids from settling; further, they may be separated or combined as a waste stream. A wide range of treatment plant configurations results in a wide range of potential Mn concentration levels in the return recycle streams in treatment plants removing Mn. In addition, the dissolved and total Mn levels are likely to be very different in each recycle stream.

Researchers in Canada (Bourgeois et al., 2004) investigated methods for treating spent filter backwash water prior to recycle and reported levels of total Mn in the backwash stream of 0.38 mg/L. In comparison, the recycle streams from two plants studied by Cornwell and Lee (1993), showed dissolved Mn levels ranging from 0.07 to 3 mg/L. In both plants the raw water Mn concentrations were in the 0.2 to 0.3 mg/L range at the time that the sludge was sampled. The impact to the Mn concentration ultimately present in the water to be treated depends on how recycle streams are managed within the treatment facility.

In a study of filter backwash recycle impacts, Tobiason et al. (2003) evaluated backwash streams from six surface water treatment plants. A summary of some of the data from that study are shown in [Table 3.3](#). These data illustrate the range of Mn concentrations that can be present in backwash recycle water under various raw water, treatment and waste processing and return flow conditions. Samples of recycled water were taken over 3 to 6 hours at each site during a recycle event.

Significantly higher levels of Mn (up to 7 – 10 mg/L) were found in the recycle stream at the Harwoods Mill Water Treatment Plant in Newport News, VA, details of which may be found in the case studies in Chapter 7.

A recommended good practice in managing recycle streams is to control recycle quantity and quality in a way that does not degrade the incoming water quality or challenge the plant treatment processes. Thus, when utilities are considering the options for recycling water containing Mn, an effort should be made to recycle at a flow rate and concentration that does not appreciably increase the raw water Mn content.

**Table 3.3**  
**Water quality results from grab samples during recycle in four treatment plants (Tobiason et al 2003)**

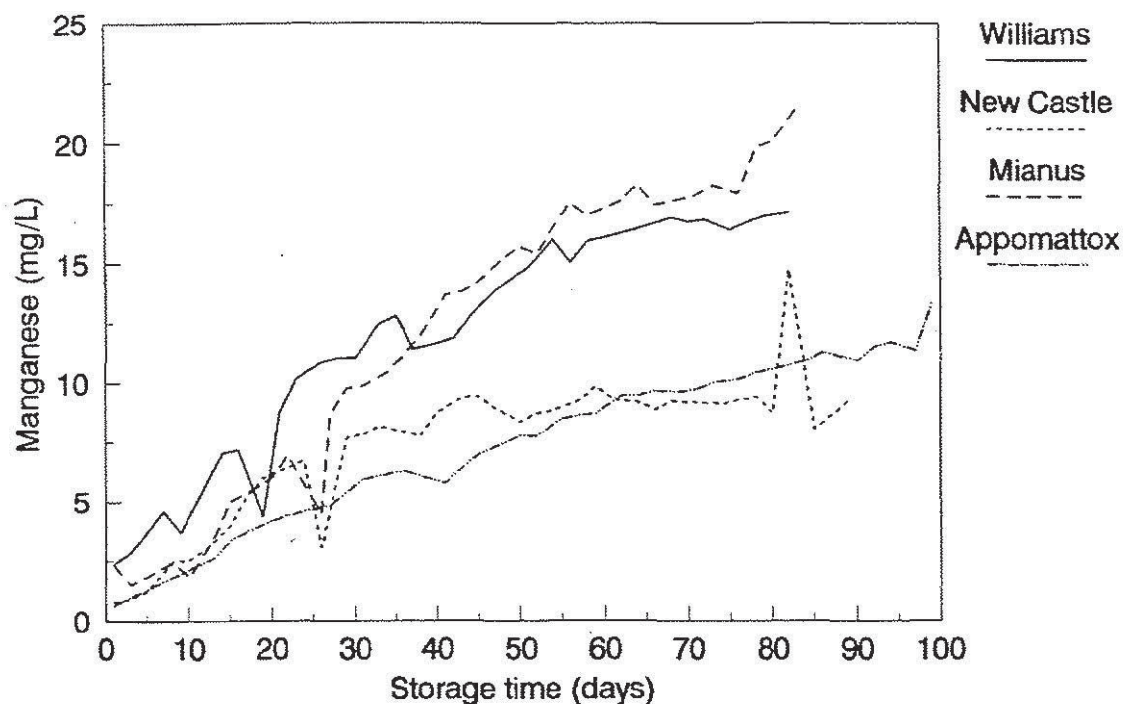
Plant	Backwash Recycle Water Processing	Raw Water Manganese (mg/L)		Recycle Water Manganese (mg/L)	
		Total	Dissolved	Total	Dissolved
E	Flow equalization	0.03	0.010	0.027-1.23	0.010-0.027
W	Flow equalization	0.14	0.011	0.10-0.86	0.008-0.086
L	22-hr settling prior to recycle	0.08	0.03	0.06-0.21	0.02-0.03
S	None	0.018	0.005	0.008-0.016	0.0098-0.01

### RELEASE OF MANGANESE FROM ACCUMULATED RESIDUALS (SLUDGE)

Much higher levels of Mn can occur in sludge solids and in decant streams from sludge clarification processes than are normally seen in filter backwash water. Cornwell and Lee (1993) reported concentrations in the sludge in clarifiers of 65 to 180 mg/L as total Mn. Dissolved Mn in the sludge waste streams was in the range of 1 to 7 mg/L.

When sludge solids are stored either in the bottom of a sedimentation tank or in a sludge solids clarifier, the release of dissolved Mn (presumably through biological processes that are active under anerobic conditions) increases the Mn content of the supernatant. The results shown in [Figure 3.6](#) are taken from Cornwell and Lee (1993) who stored several sludges in the laboratory for about three months and measured the release of dissolved Mn over that timeframe. All the sludges showed release of significant amounts of Mn, beginning almost immediately after storage was initiated, with increasing Mn levels over time.

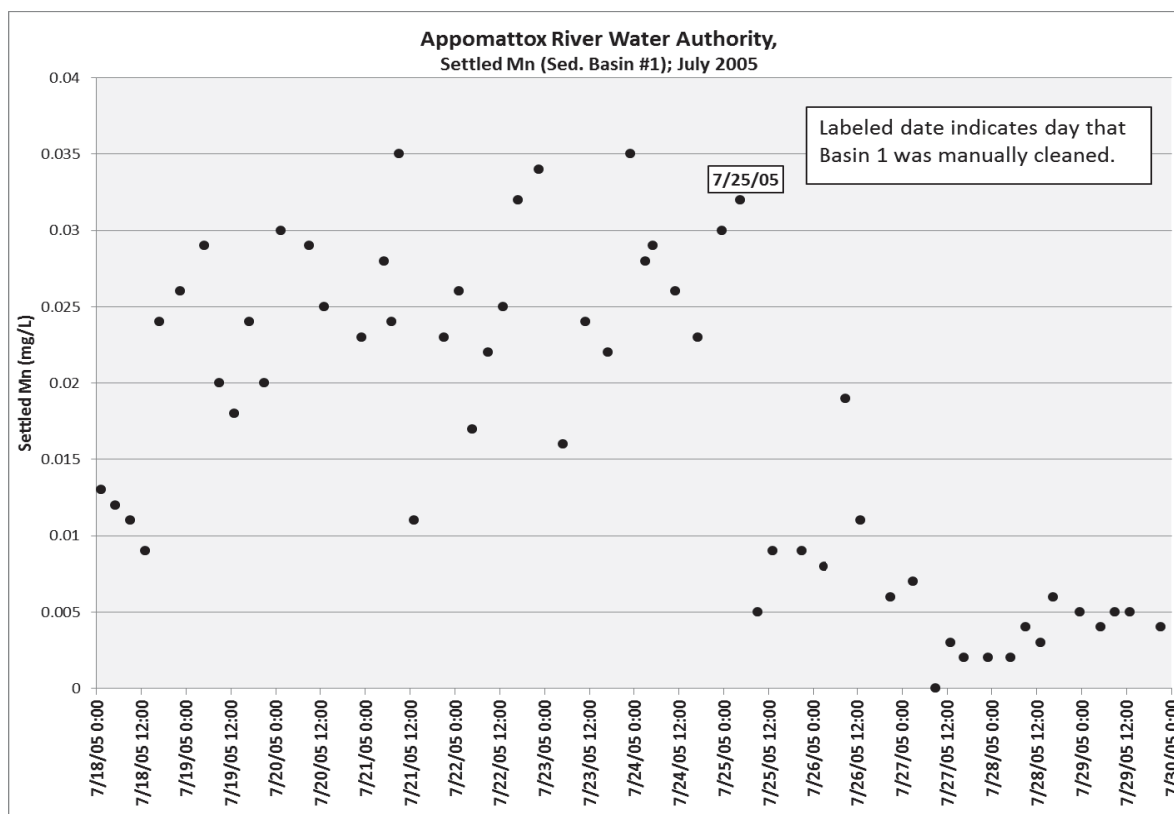




**Figure 3.6 Release of Manganese during storage from several sludges (Cornwell, D. and R. Lee, 1993)**

Similar to these laboratory results, sludge solids containing Mn that are stored in a thickener will continue to release dissolved Mn into the supernatant. Because the release of Mn from sludge solids begins within a day or two, settling basins that are manually cleaned on a monthly or quarterly basis will typically have higher dissolved Mn in the settled water between cleanings than do basins with mechanical cleaning where the sludge is removed on a daily basis.

An example of the change in level of dissolved Mn leaving a settling basin after removal of sludge can be seen in [Figure 3.7](#). This Appomattox River Water Authority plant is a conventional coagulation plant in south central VA that treats a surface water source with pre-oxidation (permanganate or chlorine dioxide during these results), alum coagulation, then flocculation and settling. This specific settling basin is one that at the time of this testing did not have solids removal capabilities; instead, the basin had to be taken offline and manually cleaned to remove accumulated solids. The plot shows dissolved Mn levels in the water leaving this settling basin as a function of time, including an indication of approximately when the basin was cleaned. The dissolved Mn level leaving the basin was more elevated before basin cleaning and decreased substantially after cleaning. A typical basin cleaning cycle in the warmer summer months was as short as 10 to 12 days due to Mn release concerns. The problem was alleviated by addition of solids removal systems in the clarifier, allowing for more continuous removal of settled solids.



**Figure 3.7 Change in dissolved manganese in settled water after manual sludge removal from settling basin**

Both laboratory and full-scale data demonstrate that the dissolved Mn content of water that has been held in a basin with Mn sludge will be highly variable, depending on the sludge detention time. This information has implications for both recycle of decant from sludge or backwash water clarifiers and for plants that do not have automated sludge removal from primary settling basins within the treatment process.

Treatment plants that are removing Mn by oxidation and settling, should make an effort to remove sludge from settling basins on a frequent basis to reduce the dissolution of Mn into the water that is passing on to the filters. If frequent removal of sludge is not possible, then treatment for Mn removal downstream of settling should be in place and operational.

For plants that store sludge and/or backwash waste water in a clarifier to allow settling of solids and decant of water to the head of the plant, decanting should take place as soon as the solids are reasonably settled to prevent dissolution of Mn into the decant water. Removal of Mn is one of several factors that argue for keeping settled sludge separate from backwash water in the management of waste streams. Backwash water may be relatively low in Mn in a plant that removes most of the Mn in settling, whereas sludge residuals, as measured by Cornwell and Lee, can be very high in Mn content. The general idea is to get the Mn solids out of the whole treatment process rather than recycling Mn, so disposal of sludge without decanting solids should be strongly considered, if the facilities to do so are available. Backwash water should be settled just long enough to remove the solids without allowing for dissolving Mn back into the recycle

stream and the recycle stream should be flow controlled so as to prevent Mn concentrations to spike in the influent to the plant.

## **OTHER RECOMMENDED RESOURCES**

Mn microbiology in groundwater: Gounot, Anne-Monique. 1994. “Microbial oxidation and reduction of manganese: Consequences in groundwater and applications.” *FEMS Microbiology Reviews* 14, 339-350.

Mn occurrence in drinking water systems: Kohl, Paul M. and Medlar, Steven J. 2006. *Occurrence of Manganese in Drinking Water and Manganese Control*. Awwa Research Foundation, Denver, CO.

## **CHAPTER 4**

### **MONITORING FOR MANGANESE**

This chapter presents the benefits of and methods for monitoring Mn in source waters and treatment facilities. The chapter includes descriptions of the analytical methods used for measuring concentrations of Mn in water. It also discusses the importance of and method for determining different forms or fractions of total Mn in a water sample<sup>1</sup>.

#### **BENEFITS OF MONITORING TO FRAME YOUR PROBLEM**

A well thought-out Mn monitoring plan can be an extremely useful tool in treating for Mn. When implemented, a good monitoring program provides both an “early warning” system for Mn events and a process control tool for treatment.

Monitoring source water allows a utility to know the variability of raw water Mn and understand whether it is dissolved, colloidal or particulate in form. Identification of Mn sources and levels of Mn provides information to assist operators in resolving treatment issues. For example, if raw water sources for a single utility differ from one another in Mn concentration, the option of diluting one source with another may be available. For utilities that have only one source of water, frequent sampling can define whether Mn levels vary seasonally, daily, or even hourly. This information will help frame the treatment solution.

Along with regular monitoring of source water for Mn, many utilities that utilize surface water supplies (especially lakes and reservoirs) monitor water quality parameters that impact raw water Mn concentrations such as DO, temperature and pH. This provides another dimension to understanding and treating a specific raw water supply.

With knowledge of the raw water Mn levels, plant staff can alter treatment and shift the monitoring approach as necessary to optimize treatment. Monitoring within the treatment plant to track Mn removal by process can identify treatment problems. This in turn can lead to adjustments that optimize Mn treatment while achieving other water treatment objectives as well.

#### **MANGANESE MONITORING IN THE TREATMENT PLANT**

The intention of water quality sampling in a treatment plant is to collect data that will assist in improving operation of the plant. When Mn is a treatment issue, parameters that provide an understanding of Mn chemistry should be included in a sampling plan. In a surface water plant, those parameters would typically include Mn, Fe, DO, pH, temperature, TOC and, in certain instances, oxidation reduction potential (ORP). In ground water plants, ammonia, reduced sulfur species and nitrite should be added to the sampling program because these

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<sup>1</sup> The form of Mn in water is a critical issue for water utilities. This is because the treatment of dissolved (reduced) Mn requires the intentional use of a suitable oxidant in the treatment process to oxidize dissolved Mn. In contrast, no additional action may be required by a utility to treat particulate Mn since particulate Mn is inherently removed during treatment if a solid/liquid separation process is a part of the existing treatment train.



constituents can impact the oxidation of Mn. Any other parameters that are expected to be present that compete for oxidant demand should be included in a sampling program. The measurement of Mn should include fractionation of Mn into particulate, colloidal and dissolved forms.

Typically, all parameters are monitored in the influent raw water. Keep in mind while planning sampling programs that analysis must occur before reactions take place that can alter the parameter(s) of interest. Parameters that should be measured in the field include any that could be altered by reactions with oxygen in the air. For example, water samples should be filtered by hand-held filters at the well head to obtain an accurate measurement of Fe and Mn speciation; further, pH should always be measured in the field within 15 minutes of sample collection.

Selection of locations for sampling particular parameters within the treatment plant processes are plant-specific. By measuring Mn after settling and filtration, plants can determine where in the treatment process train the Mn is being removed (or not removed) so that treatment can be adjusted appropriately to optimize Mn removal. Measurement of Mn in backwash return flows or decant from settling basins is essential for understanding the impact of those return flows on overall mass loading of Mn as well as Mn removal in treatment.

The frequency of measurement is dependent on the historical knowledge of Mn at the plant and is different at each plant. For example, surface water plants that draw raw water from reservoirs might want to plan daily or even hourly sampling during the seasons when Mn concentrations are likely to be changing relatively frequently. During winter months, when surface water typically does not experience drastic changes in Mn concentration, weekly monitoring may be sufficient. Ground water plants may find that levels of Mn are relatively stable in raw water. However, not all ground water sources have consistent Mn concentrations. As such, weekly or daily monitoring may be necessary to build a sufficient historical data base to define variability. Overall, utilities should not assume that Mn levels are stable over time until sufficient data has been collected to prove that this is the case.

Monitoring data should be reviewed after each sampling event to determine whether water quality is changing so that appropriate treatment decisions can be made based on early warning data. Using measured Mn concentration to control oxidation can be challenging if the raw water Mn concentration varies on an hourly or shorter basis.

An alternative option for controlling oxidant doses for Mn removal is the use of an oxidation-reduction potential (ORP) analyzer. Use of ORP for dose control has worked for some utilities, but has not been helpful for others. This approach requires development of a correlation between ORP readings and Mn removal that is plant specific. Maintenance of ORP probes is a daily requirement to prevent build-up of  $MnO_x(s)$  deposits which affect the operation of the probe. The use of this technology is discussed in detail in Chapter 7 as part of the Westminster, CO, case study.

Fractionation should be performed on all Mn samples to measure the particulate, colloidal and dissolved Mn. Particulate Mn is typically operationally defined as Mn retained by a 0.45 to 1 micron filter. Mn that passes through the particulate filter but is retained by a 10,000 to 30,000 apparent molecular weight cutoff (MWCO) ultrafiltration membrane is operationally defined as colloidal Mn. Dissolved Mn is defined as the Mn passing through the ultrafiltration membrane. Knowledge of the form of Mn present is critical in determining whether the

treatment approach should focus on oxidation or on particulate removal processes. Table 4.1 summarizes the significance of the form of Mn in water samples. (Fractionation is discussed in more detail in the next section.)

**Table 4.1**  
**Significance of the form of manganese in water**

Mn Form	Characteristic	Description	Presence in Raw Water Indicates	Presence in Treated Water Indicates
Particulate	Mn retained by 0.45 to 1 micron filter	Oxidized form of Mn which can be readily removed by coagulation and subsequent solid-liquid separation processes	Oxidation of Mn not required, Mn should be removed by solid-liquid separation processes	Sufficient oxidation and coagulation of Mn has occurred; focus on improving solid-liquid separation processes
Colloidal	Mn retained by 10,000 to 30,000 MWCO filter	Oxidized form of Mn which requires destabilization and coagulation prior to removal by solid-liquid separation processes	Oxidation of Mn not required prior to solid-liquid separation processes.	Sufficient oxidation of Mn has occurred; focus should be on improved destabilization, coagulation and solid-liquid separation.
Dissolved	Mn passing through 10,000 to 30,000 MWCO filter	Unoxidized form of Mn which will oxidize in distribution system and result in consumer complaints	Complete oxidation of Mn required for successful treatment when depending on solid-liquid separation processes for Mn removal.	Insufficient oxidation of Mn has occurred; additional oxidant, contact time or higher pH required.
Total	Mn of unfiltered sample	Total Mn in sample	When present at > 15 µg/L treatment required.	Risk of customer complaints at > 15 µg/L; additional treatment required

## MANGANESE MONITORING IN RESERVOIRS

Sampling in supply reservoirs should be planned to include all relevant water quality parameters that govern changes in Mn in the reservoir, as well as those which can impact treatment optimization at the plant. Parameters for sampling include Mn, iron, DO, pH, temperature and TOC. If there are suspicions that nitrite or ammonia may be present, they should be included in the sampling.

Monitoring water quality in water supply reservoirs can provide early warning of major changes in water quality that may affect the water treatment plant and treated water quality. Along with the sampling results, plant staff should be aware of typical travel times from the reservoir sampling sites to the treatment plant so that use of data for early warning purposes is timed properly.

A plan for reservoir sampling must be tailored to staff availability and access to sampling sites. Typically, plants that use large reservoirs as sources have access to or own a boat so that staff can sample at the same location in the reservoir during each sampling event. Locations in

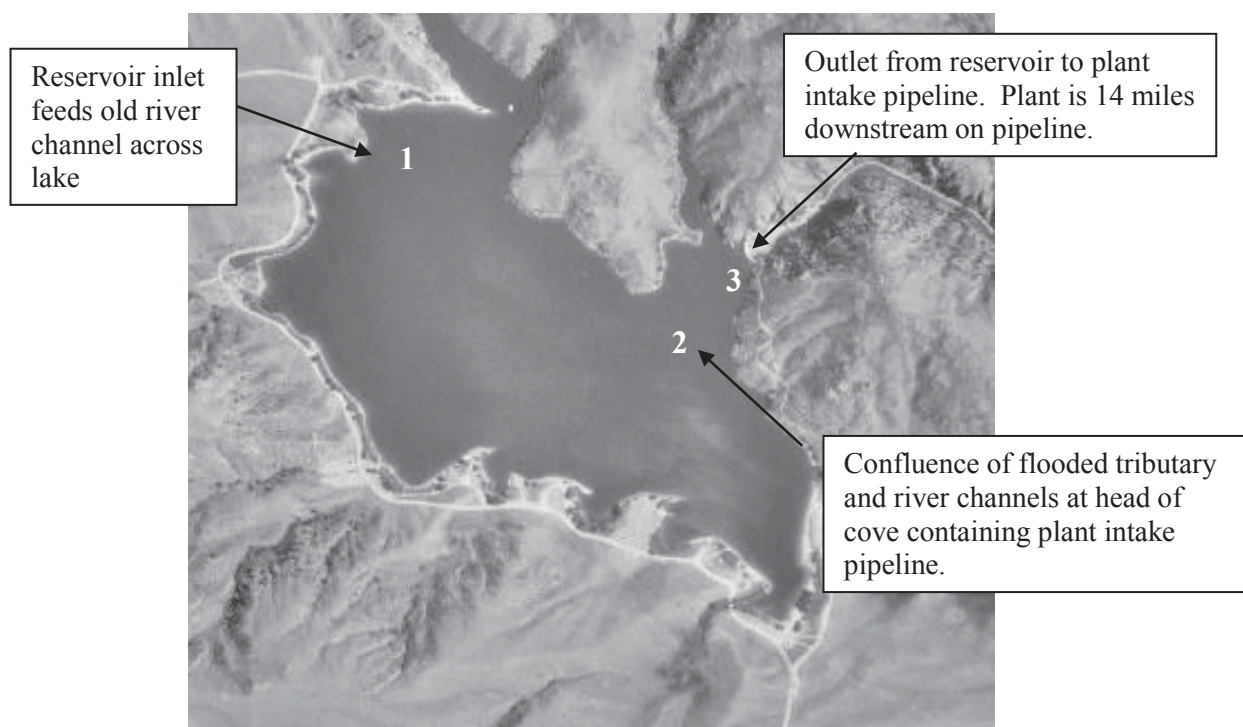
the reservoir should be established to capture information at the reservoir outlet, at a location representative of the normal flow path through the lake and at or near the inlets. Using a GPS locator to find the same location on the lake for taking samples is useful. Sampling at these locations provides an understanding of water quality entering the lake, leaving the lake and at some mid-point(s) in the flow path across the lake.

Another way of determining lake sampling sites is to select an early warning site (area of lake inflow), an intermediate warning site (half the flow time to the plant intake) and a short-term warning site (where the water is leaving the lake and entering the plant). Locations of the sample points should be reviewed with water quality staff prior to initiating sampling in order to refine the locations based on previous sampling experience.

## **Recommended Sampling**

At each sampling site and each sampling event, a reservoir profile should be taken so that water quality parameters are measured at the surface, at the bottom and at selected regular intervals across the depth of the reservoir. The depth intervals selected depend on the overall depth of the lake and what is known about the typical seasonal depth of the hypolimnion. During the first year of sampling, depth sampling sites might be established at intervals representing a quarter of the total depth with a couple of extra sampling depths selected in the bottom quarter. The objective of this sampling arrangement is to determine the approximate depth at which the hypolimnion forms. Once a few years of data are available, the depth of each profile site could be shifted to reflect the typical depth of hypolimnion development and to maintain sufficient data to understand how the lake water quality is changing.

Geographic location of sampling sites depends on the configuration of the reservoir. Most plants want to know the profile at 3 to 4 sites, depending on the size of the reservoir. Locating a sample site near the outlet from the reservoir to the treatment plant provides some direct information about the water quality that can be expected at the plant. Other likely sample sites would be located along flow paths through the lake or near inlets to the lake. Often a reservoir is located along an old river channel and the major flow pattern through the lake can be expected to pass along that same flow path. An example of sample site selection is shown in [Figure 4.1](#), where the sampling sites reflect inflow into the lake (site 1), a point along the old stream channel in the where a tributary joined the flooded river channel (site 2) and the outlet to the treatment plant (site 3).



**Figure 4.1 Three sampling locations along old stream channel in Crystal Lake, WY**

Parameters to sample include DO, temperature, dissolved and total Mn, dissolved and total Fe and turbidity. Measurement of colloidal Mn in raw water is not necessary since colloidal Mn does not normally form unless a strong oxidant is present. Utilities that do regular sampling in reservoirs often include algae counts (types should be tailored to species that are typically present) in their analysis of water samples. While algae counts don't offer direct information about Mn concentration in the water, they do provide some understanding of the shift in nutrient levels in the water. Since nutrients can be mobilized from the soil along with Fe and Mn, algae counts indicate water quality changes of interest in tracking Mn.

Lake water quality profiles should be completed on a regular basis during periods of water quality changes. For reservoirs in colder climates, sampling schedules will typically run from April through October, covering the runoff season and the development of stratification and turnover. In southern climates, sampling may continue throughout the year since there might be biological parameters of interest (algae blooms) at any time of year.

The interval between sampling events may change at different times of the year. During the period when thermal stratification is developing, sampling on a weekly basis will ensure that the stratification is well defined. At other periods, sampling might occur bi-weekly or even monthly to provide seasonal data continuity.



## Use of Data

All data collected by these samplings should be reviewed on a regular basis and compared to historic levels. Any changes to water quality should be investigated. Lake profiles can be compared to raw water quality at the plant in order to develop an early warning system for situations related to elevated Mn concentrations. The location and frequency of the lake profiles should be refined based on the data and the treatment needs of the plant.

## MANGANESE ANALYTICAL METHODS, SIZE FRACTIONATION

Effective control of Mn in water treatment facilities requires information related to both the concentration as well as the forms of Mn present. Mn is able to exist in a variety of valence states in water. Dissolved Mn is typically present as either the reduced Mn(II) form or, in highly oxidized environments, as the Mn(VII) form of the permanganate ( $\text{MnO}_4^-$ ) ion. Insoluble Mn can be present in multiple types of solids. In alkaline waters of substantial alkalinity there is the potential to form manganous carbonate ( $\text{MnCO}_3(\text{s})$ ) due to its limited solubility in water. However, in most water treatment situations, oxidants are either present (e.g., DO) or added (e.g., potassium permanganate, chlorine dioxide, ozone) to yield oxidation of the Mn(II) to either Mn(III) or Mn(IV). Both valence states of Mn are highly insoluble in water, leading to the precipitation of various  $\text{MnO}_x(\text{s})$  solid phases. Particulate Mn may also be present in water due to the presence of oxidizing bacteria that house oxidized  $\text{MnO}_x(\text{s})$  solids within their cell structure.

Knowledge about the forms of Mn present in a water sample is very important when considering the most effective methods for Mn control in drinking water operations. Reduced, dissolved Mn(II) is typically addressed by (a) the addition of strong chemical oxidants to promote bulk solution oxidation of the dissolved Mn(II) to  $\text{MnO}_x(\text{s})$  (which is then removed by solid-liquid separation methods); (b) sorption of dissolved Mn(II) onto  $\text{MnO}_x(\text{s})$ -coated filter media; or (c) biologically-based oxidation of dissolved Mn(II). In contrast, particulate Mn (typically present as a  $\text{MnO}_x(\text{s})$  solid phase) requires none of these treatment methods and, instead, is addressed most effectively by conventional solid-liquid separation techniques (e.g., coagulation/flocculation, clarification and/or filtration).

Unfortunately water utilities often do not differentiate between particulate and dissolved species when quantifying Mn concentrations within the water treatment plant. Instead, the convention is often to quantify and report only the total Mn concentration. Total Mn content does not allow for decision making regarding appropriate Mn control methods; rather, knowledge of dissolved and particulate Mn concentrations is essential to differentiate between needs for more effective oxidant dosages (if, for example, chemical oxidation is being practiced for dissolved Mn(II) control) versus more effective solid-liquid separation.

One of the specific challenges in fractionating Mn into different forms is the presence at times of “colloidal”  $\text{MnO}_x(\text{s})$  solids, solids that are of a characteristic size such that they will readily penetrate through glass fiber (nominal 1  $\mu\text{m}$ ) or similar (e.g., 0.45  $\mu\text{m}$ ) filters. Such filters are very commonly used to quantify the “dissolved” concentration of analytes in solution. However, researchers have shown that the use of strong oxidants such as potassium permanganate ( $\text{KMnO}_4$ ), chlorine dioxide ( $\text{ClO}_2$ ) and/or ozone ( $\text{O}_3$ ) for dissolved Mn(II)

oxidation can generate byproduct  $\text{MnO}_x(\text{s})$  solids that are highly colloidal in nature and possess sizes too small to be captured by the traditional filters used in water analysis methods. These colloidal  $\text{MnO}_x(\text{s})$  solids are more prevalent when dissolved  $\text{Mn}(\text{II})$  is oxidized in low-hardness waters as divalent  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations help to aggregate colloidal  $\text{MnO}_x(\text{s})$  solids into particles of sufficient size to be retained by these standard analytical filters.

The presence of colloidal  $\text{MnO}_x(\text{s})$  solids can lead to misinterpretation of the analytical results obtained for Mn. When colloidal materials pass through the analytical filter they will end up being quantified as part of the dissolved Mn fraction in a water sample and presumed to be in the  $\text{Mn}(\text{II})$  form. If the dissolved Mn measurement is thus elevated due to their presence, then a decision may be reached that insufficient chemical oxidant is being added to the water sample during treatment and the oxidant dosage may be increased in response. The additional oxidant will not address the treatment deficiency as the dissolved Mn has in fact already been oxidized to the colloidal  $\text{MnO}_x(\text{s})$  solids; hence, more oxidant is added than necessary when the correct treatment response would be to add more coagulant to destabilize and aggregate the colloidal  $\text{MnO}_x(\text{s})$  solids into particles of sufficient size that they can be effectively removed in the treatment plant.

Ozonation of water containing Mn can occasionally lead to the formation of a small amount of permanganate if the ozone dosage is well above the stoichiometric amount for  $\text{Mn}(\text{II})$  oxidation. Any permanganate formed would readily pass through an analytical filter and ultimately be quantified as “dissolved Mn” and, most likely, misinterpreted as unreacted, reduced  $\text{Mn}(\text{II})$ .

### **Sample Collection and Preparation for Analysis**

As with all contaminants, care should be taken when sampling Mn. The sample location should be representative of the water quality being tested and water quality should not be influenced by the sampling process. Sample taps should be rinsed 3-5 minutes prior to sampling to assure a representative sample. Acid rinsed (1+1 nitric acid) polyethylene or equivalent plastic container should be used for the Mn sample. When collecting the sample, the container should be rinsed with sample water at least three times prior to sample collection. The sampler should wear gloves and take care to prevent contamination of the sample during the sampling process.

In the absence of oxidizing agents (e.g., free chlorine, potassium permanganate, ozone, chlorine dioxide) dissolved  $\text{Mn}(\text{II})$  is reasonably stable in solution. However, it is good standard practice to filter samples as soon as possible after collection to help ensure an accurate differentiation between dissolved  $\text{Mn}(\text{II})$  and oxidized, particulate  $\text{MnO}_x(\text{s})$  species. Samples that have not been exposed to strong oxidizing agents typically do not have colloidal  $\text{MnO}_x(\text{s})$  species present; as such, use of a standard glass fiber (0.45  $\mu\text{m}$  or 1  $\mu\text{m}$ ) filter paper can be sufficient for insuring capture of particulate Mn species. Alternatively an appropriately sized cartridge filter attached to a syringe can be used. If strong oxidants have been added to the sample, then the potential exists for colloidal  $\text{MnO}_x(\text{s})$  form to be present. In such situations passage of the sample through an ultrafiltration membrane may be required to ensure capture of these colloidal solids. If an ultrafiltration membrane is not available then coagulation of the water sample with aluminum sulfate (alum) followed by glass fiber filtration will minimize the

penetration of colloidal  $\text{MnO}_x(\text{s})$  into the filtrate, helping to ensure a more accurate determination of the dissolved Mn concentration in the sample<sup>2</sup>.

Analysis for particulate Mn content in water samples may require digestion of the sample prior to the actual analytical procedure. Guidance should be sought from Standard Methods (Method 3030-A) regarding the possible need for digestion. Samples that are colorless and transparent and have a turbidity  $<1$  NTU may be analyzed directly for total metals without digestion. Otherwise, digestion in a strongly acidic environment ( $\text{pH} < 2$ ) for several hours is required to help ensure conversion of particulate Mn into dissolved forms.

All water samples for future Mn analysis should be acidified with 1% trace metal nitric acid after collection and filtration prior to storage.

## Mn Analysis Methods

Multiple options exist for quantifying the concentration of Mn present in water. These are described in the sections below.

### *Colorimetric Methods*

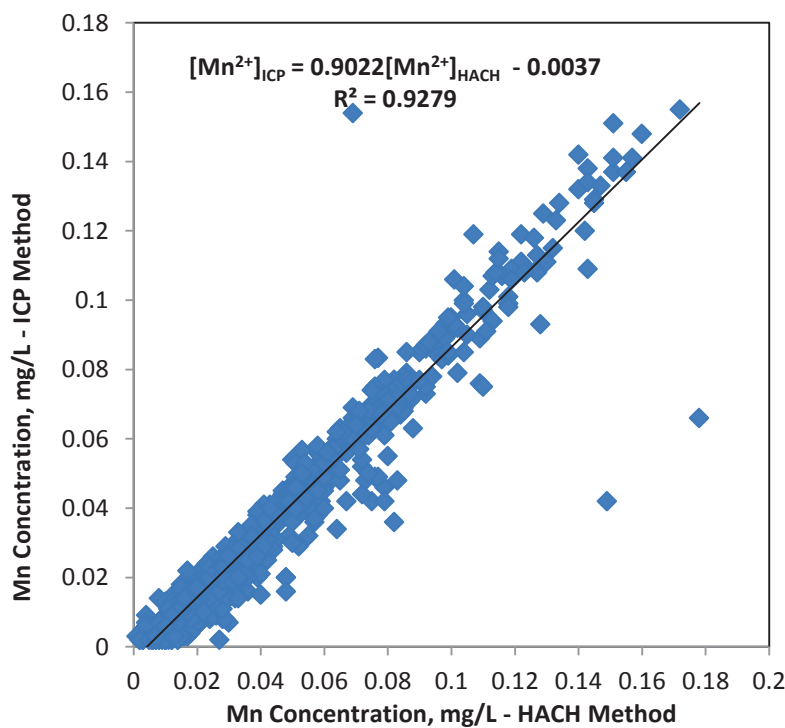
Several different colorimetric methods exist for quantifying Mn. Because these methods often rely on the reaction of Mn with other compounds, the procedures are subject to interferences that may ultimately affect the accuracy of the analysis. Depending on the method used, other metals or organics in solution may interfere with the measurement of Mn. However, these methods do have the advantage of being relatively inexpensive and require only a few chemical reagents and a simple spectrometer to perform the analysis.

One method involving the use of persulfate yields a method detection limit of roughly 50 ppb (Standard Methods, Method 3500-Mn B). Another proprietary method developed by the Hach company employs ascorbic acid, alkaline cyanide and an indicator solution and is reported to be able to detect Mn concentrations as low as 10 ppb. This technique is often employed by water utilities seeking to monitor for Mn concentrations within their treatment facility for operational control purposes. One research study evaluated split samples for Mn concentration between this Hach procedure and inductively coupled plasma (ICP) spectrometry and found a very good correlation ( $R^2 > 90\%$ ) between the two analytical results as shown in [Figure 4.2](#), although the Hach method tended to report slightly greater concentrations than the ICP. None the less, this was a very useful outcome as the Hach technique is well suited to use in “real-time” operational control testing for process monitoring. While other methods (described in subsequent sections) would be required for regulatory compliance monitoring, the ability to use methods of this type for effective “real-time” process monitoring is important. But it should be emphasized that while colorimetric methods are very useful in gauging trends they do not necessarily indicate the true Mn concentration. Utility personnel using Hach or other colorimetric methods for process monitoring should establish a quality control program with

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<sup>2</sup> Alum will coagulate colloidal Mn allowing it to be captured by the glass fiber filter while causing minimal change to the dissolved  $\text{Mn}^{2+}$  concentration.

occasional split-sample analyses using ICP or other compliance-approved methods to help ensure a reliable correlation between the two methods.



**Figure 4.2 Distribution of pilot-scale dissolved Mn concentration values analyzed by Hach and ICP methods**

There are occasions where knowing the valence state of Mn present may be of interest. In such instances the leucoberberlin method can be used as this colorimetric technique will differentiate Mn(II) from other oxidized Mn species. The procedure involves addition of a small amount of leucoberberlin blue to the sample under a mild acid environment. A colorimetric response is produced in direct correlation to the amount of oxidized Mn present. The concentration of oxidized Mn can then be quantified by comparing the absorbance of the sample (at 620 nm) to a standard curve prepared using various concentrations of potassium permanganate (KMnO<sub>4</sub>).

### ***Flame Atomic Absorption (AA)***

Flame atomic absorption spectrometers vary somewhat in their specific configurations, but all instruments have a few components in common. All AA spectrometers utilize a source of spectral radiation which is often generated using a cathode lamp. With older spectrometers, a specific lamp must be manually loaded into the instrument in order to analyze one specific element. The resulting spectrum is then passed through a flame that is generated using a combination of acetylene gas and air. The liquid sample containing Mn is fed into the instrument and passes through a nebulizer which converts the liquid into a fine mist. The interaction of the sample with the flame causes the Mn in the sample to briefly atomize. These



excited atoms of Mn then interact with the spectrum generated by the cathode lamp and absorb a portion of the spectrum's intensity as the beam passes through the flame and reaches the detector. The Beer-Lambert Law is then applied to determine the concentration of Mn in the sample. By analyzing a series of solutions with known concentrations of Mn, a linear relationship between absorbance and concentration can be determined. While the instrument itself is costly, the cost per analyzed sample is low. The instrument detection limit for Mn using AA is roughly 10 parts per billion (ppb). (Standard Methods, Method 3111A).

### ***Inductively Coupled Plasma Mass Spectrometry (ICP-MS)***

ICP-MS offers better analytical sensitivity than AA, but at an increased cost of analysis. ICP-MS also allows the user to simultaneously quantify concentrations of many different metals; unlike AA which generally only allows for the measurement of a single metal per analysis. During operation the instrument draws up a portion of the sample and injects it into a nebulizer. The sample then interacts with the high temperature plasma generated by the instrument. Atoms present in the sample are vaporized and subsequently ionized by the plasma by giving up a single electron in order to form monovalent cations. The ions then move on to the mass spectrometer where they are passed through a series of conical detectors that quantify the amount of each element present in the sample. Quantification is achieved by comparing the measured detector signals of known calibration standards to water samples containing a particular element. The instrument requires argon gas in order to maintain the plasma which heightens the analytical cost of each measured sample. The instrument detection limit for Mn using ICP-MS is 0.002 ppb (Standard Methods, Method 3125B).

### ***Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-ES)***

A second ICP option is ICP atomic emission spectroscopy (ICP-AES), also known as ICP optical emission spectrometry (ICP-OES). Similar to ICP-MS, an injected aqueous sample interacts with an argon gas maintained plasma. However, instead of detecting atomic mass as in ICP-MS, the intensity of electromagnetic radiation emitted by the plasma excited atoms is measured using ICP-AES. Simultaneous or sequential multiple element measurements are possible, also similar to ICP-MS. The instrument detection limit for Mn using ICP-AES is higher than for ICP-MS but lower than for AA, at roughly 2 ppb (Standard Methods, Method 3120B).

## **OTHER RECOMMENDED RESOURCES**

Standard Methods 20<sup>th</sup> Edition. 3500-Mn B. Persulfate Method

Standard Methods 20<sup>th</sup> Edition. 3111 Metals by Flame Atomic Absorption Spectrometry – 3111 A

Standard Methods 20<sup>th</sup> Edition. 3030-A Sample Digestion Procedures

EPA METHOD 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry - Revision 5.4 - EMMC Version Stein, L.Y., La Duc, M.T., Grundl, T.J. and Nealson, K.H. (2001)

Bacterial and archaeal populations associated with freshwater ferromanganous micronodules and sediments. Environmental Microbiology 3(1), 10-18.



## CHAPTER 5

### SOURCE WATER MANAGEMENT FOR MANGANESE CONTROL

In some instances, viable options are available for minimizing the level of Mn in water treatment plant (WTP) influent. This chapter describes opportunities for managing ground water and surface water sources to achieve that goal.

#### GROUND WATER SOURCE MANAGEMENT

Water from an individual ground water well typically has a fairly consistent Mn concentration. However, many utilities use multiple wells for the water system supply, so even though each well may have a consistent Mn concentration, differences between wells can be fairly common. An example well field in Nebraska (discussed in Chapter 3), consisting of nine wells all within sight of one another, has reported Mn levels across all the wells from <0.1 µg/L to 430 µg/L. For systems similar to this one, the obvious source water management approach to control Mn levels is to selectively pump different combinations of wells at different rates to provide a blended water that has manageable Mn levels.

A flow-weighted calculation for Mn concentration can be used to determine the amount of water to withdraw from each well to meet a target blended water Mn level. The Mn values used for each well in the calculation should be the Mn concentration in the raw water. The calculation could be set up in a spreadsheet format with cells that can be changed for the flow and raw water Mn concentration at each well. An example formula for the case of three wells is:

$$[(Q_{\text{Well1}} \times \text{Mn}_{\text{Well1}}) + (Q_{\text{Well2}} \times \text{Mn}_{\text{Well2}}) + (Q_{\text{Well3}} \times \text{Mn}_{\text{Well3}})] / (Q_{\text{Well1}} + Q_{\text{Well2}} + Q_{\text{Well3}}) = \text{Mn}_{\text{Blend}}$$

Where:  $Q_{\text{Well1}}$  = Flow in gpm from Well 1 (similar for Well 2 or Well 3)

$\text{Mn}_{\text{Well1}}$  = Mn in µg/L in Well 1 raw water (similar for other wells)

$\text{Mn}_{\text{Blend}}$  = Mn in µg/L in the blended well water

Using this type of calculation allows a ground water system operator to determine which combinations of wells can be operated and at what flows to produce a specific Mn concentration in the blended water prior to treatment. The ability to blend water to control Mn concentration contributes to more reliable treatment that is easier to operate because the variability of raw water Mn is reduced.

#### SURFACE WATER SOURCE MANAGEMENT BY AERATION

##### Hypolimnetic Aeration

Water systems utilizing surface water that is stored in reservoirs or lakes must deal with a number of water quality concerns that arise from nutrient enrichment of the water and increased levels of biological activity. Hypolimnetic anoxia (complete loss of DO in the hypolimnion) is a common occurrence in lakes that thermally stratify for a portion of the year. Factors affecting the development of the anoxic zone in the hypolimnion are addressed in Chapters 2 and 3. In

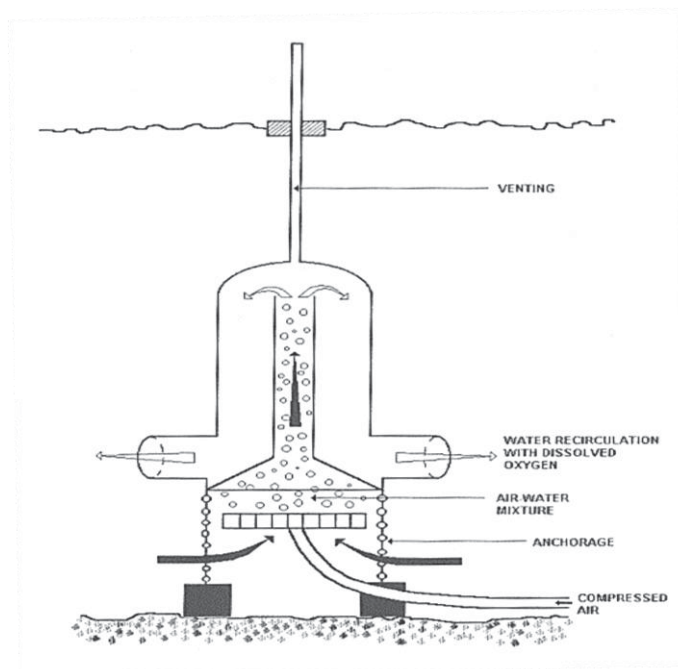


general, nutrient levels (trophic state), the loading of organic matter, temperature and volume of the hypolimnion (particularly relative to the lake bottom sediment area) are factors that impact the rate of DO depletion in the bottom water. The result of hypolimnetic anoxia is the increased solubilization of reduced species ( $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , sulfide and ammonia) and their diffusion into the water column, where they can be transported to a treatment plant intake and withdrawn for treatment. In addition to the water quality problems associated with high levels of Mn, treatment plants can be faced with taste and odor concerns and overall increased oxidant demand due to anoxic conditions.

One method of managing raw water Mn in reservoirs is to provide adequate DO in the hypolimnetic layer of the reservoir to minimize solubilization from the bottom sediments. Hypolimnetic aeration and oxygenation are commonly used to add DO to reservoirs while preserving stratification. The three primary devices used to add oxygen to the hypolimnion are the airlift aerator, Speece Cone and bubble-plume diffuser. Each of these devices generates a stream of gas bubbles in contact with water to facilitate the transfer of oxygen to the water. Model predictions of the transfer of oxygen (along with nitrogen and other soluble gases that may be present in the bubbles) using any of these devices are typically based on the behavior of individual bubbles.

As shown in [Figure 5.1](#), airlift aerators operate by injecting compressed air near the bottom of the hypolimnion. Inside the aerator which is installed on the bottom of the lake, the air-water mixture travels up a vertical tube to a specific depth in the lake from which the remaining gas bubbles are vented through a pipe to the surface. The oxygenated water is returned to the hypolimnion through return pipes. Air is typically supplied from compressors located on shore through feed lines to the center of the unit.

The Speece Cone is a submerged downflow bubble contactor in which oxygen is injected into an enclosed cone-shaped chamber located in the hypolimnion. Water and oxygen gas are introduced at the top of the cone so that the downward velocity inside the cone is sufficient to overcome the rise velocity of the bubbles. The water flow rate and slope of the walls control the water velocity and the time available for gas transfer inside the chamber. The resulting oxygenated water is discharged to the hypolimnion through diffusers. A photograph of a Speece Cone prior to installation is shown in [Figure 5.2](#).



**Figure 5.1 Conceptual drawing of an air-lift aerator**



**Figure 5.2 Speece Cone prior to installation at Marston Reservoir, CO. (Photo S. Clark)**

Bubble plume diffusers can be linear or circular and can inject either air or oxygen at a relatively low gas flow rate. Bubble plume diffusers work best in deep lakes where the bubbles dissolve in the hypolimnion and the momentum generated by the bubble plume is low enough to prevent alteration of the thermocline. Gas bubbles are injected into the water column through a porous diffuser, creating a gas/water mixture that rises. The plume rises until the vertical density gradient causes it to stop, with the oxygenated water falling back to an equilibrium depth. The oxygenated plume then spreads horizontally within the hypolimnion. If the diffusers are

correctly located in the deepest portion of the lake, the oxygenated water will spread out and supply oxygen to the bottom sediments.

When a bubble plume diffuser is fed from a liquid oxygen (LOX) system, the vaporized oxygen is at sufficient pressure to overcome the pressure required to be injected through the diffuser into the bottom of a deep lake. This eliminates the need for compressors and greatly simplifies the design of the aeration system. No electrical power is needed to vaporize LOX to gaseous oxygen since the heat exchanger which performs this function draws heat from the surrounding air. Electrical power is only required at the site for instrumentation, control, security or lighting. Hence LOX systems are very well suited for installation at remote locations.

Liquid oxygen is stored in large pressure tanks that can be located outside year-round without protection from the weather. Delivery of LOX is similar to delivery of other bulk chemicals in that the vendors use 80,000 pound tractor trailer trucks to deliver typical 5,000 gallon (47,500 pounds) LOX loads. Generally, the valves, piping, heater and vaporizer are all supplied along with the tank by the LOX supplier. Piping from the LOX tank to the lake shore can be direct-buried similar to any chemical pipeline or it can be attached to the face of a dam and be routed up and over the dam to the bottom of the reservoir on the water side of the dam.

Piping in the lake is installed by floating a pair of pipes (one for gas and one for buoyancy) into position on the lake and then sinking the set by filling the buoyancy pipeline with water (see [Figure 5.3](#)). The oxygen diffusers are attached to the air line at regular intervals and are fed independently of one another, so if one section of diffuser fails, the remainder of the plume is still active.



**Figure 5.3 Surface deployment of bubble diffuser lines prior to sinking at Crystal Lake, WY (Photo P. Brandhuber)**

The amount of oxygen required to aerate the hypolimnion of a lake can be estimated based on the volume of water in the hypolimnion, seasonal measurements of the DO profile in the lake and results from sampling bottom sediments to determine the oxygen demand of the sediment. A bathymetric survey is essential for estimating the volume of hypolimnetic water and for laying out a bubble plume system in the appropriate location in a lake. Sediment oxygen

demand can be highly variable and difficult to estimate. These estimates should only be performed by experienced designers of aeration systems.

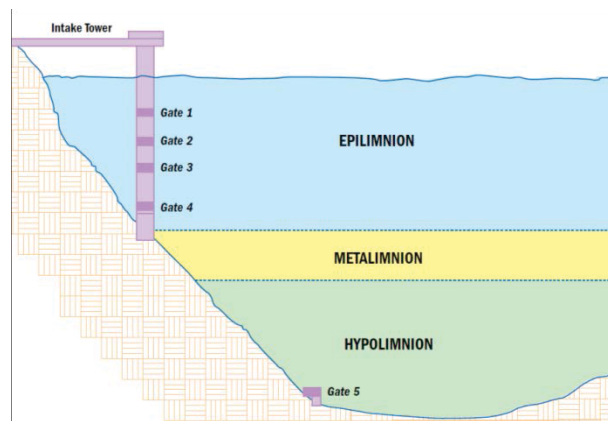
### Complete Reservoir Mixing

Aeration equipment is also available that will mix the entire depth of a reservoir. These units draft water from lake bottom layers through an induction tube to the top of the lake where it is released. They can be powered through a cable connection to the shore.

Complete destratification of a lake brings oxygenated surface water to the bottom of the lake, reducing the mobilization of Mn from the sediments. Complete mixing will also eliminate the thermocline, making all the water roughly the same temperature. Any algae growing near the surface will be mixed into the water at depth, so algae may reach a water plant intake that is located in the hypolimnetic layer of the lake. By mixing the full lake depth, chances are significantly increased that algae or taste and odor compounds will be drawn into a deep raw water intake, thereby creating a treatment problem that may not have existed previously.

### OPERATIONAL USE OF MULTI-LEVEL INTAKE

Some surface water treatment plants that withdraw source water from deep reservoirs have a multi-level intake. This situation allows operators to select the level in the reservoir from which to draw water into the plant. Of course, the elevation of each intake is set at the time of design/construction of the facility, along with the number of gates, which can range from two to five depending on the depth of the reservoir. A schematic diagram of a reservoir with multiple level intakes is shown in [Figure 5.4](#).



**Figure 5.4 Example multi-level water treatment plant intake (Benskin, P. and K. Linder 2004 Reprinted from *Opflow* by permission. Copyright © 2004 by the American Water Works Association).**

Selection of an intake level to use is based on a number of parameters, one of which is Mn concentration. If minimizing Mn is the major objective, the obvious strategy is to monitor dissolved Mn (and DO) at each intake and take water from the level with the least dissolved Mn



(or highest DO) in the water or to selectively take water from multiple intakes as a blend to reach Mn levels that are treatable by the processes present in the water treatment plant.

Some utilities use other criteria than dissolved Mn levels to determine which intake to operate. When a reservoir becomes anoxic in the hypolimnion, nutrients tend to build up near the bottom sediments. If the hypolimnion remains static (no water is withdrawn) over the summer season, the concentration of nutrients at the bottom is released to the upper levels of the reservoir at the time of turnover. This extra load of nutrients in the epilimnion can foster increased algae blooms with accompanying taste and odor problems.

One example of a system with dual intakes is the City of Westminster (see Chapter 7 for case study). Westminster has elected to use its lower intake year around because Westminster knows it can treat the Mn that occurs in the lower portion of its reservoir and it wants to minimize taste and odor events, which it finds more difficult to treat than Mn given the existing plant configuration. As reported in AWWA *Opflow*, the City of Aurora, CO uses its lowest intake in the spring and early summer until Mn levels become too high to treat at the utility's direct filtration plant. Then Aurora opens a second, higher intake gate to blend epilimnetic water with hypolimnetic water to reach a Mn concentration that is operationally acceptable. In this manner Aurora continues to withdraw high nutrient water from the bottom of the reservoir for as long as possible prior to lake turnover in the fall, reducing the amount of nutrients which will be made available for algae growth in late summer and fall after turnover.

## OTHER RECOMMENDED RESOURCES

Mobley Engineering, Inc., Norris, TN, for design of bubble plume diffuser systems fed from liquid oxygen systems.

Benskin, P. and Linder, K. "Hypolimnion Withdrawal Renews Reservoir." *Opflow*. AWWA. May 2004, p. 12-15.

Singleton, V. L. and Little, J. C. "Designing Hypolimnetic Aeration and Oxygenation Systems – a Review" *Environ. Sci. Technol.* 2006, 40, 7512- 7520.

## CHAPTER 6

### TREATMENT TECHNOLOGIES FOR MANGANESE REMOVAL

#### OVERVIEW OF APPROACHES

As described in Chapter 5, several strategies can be employed to limit or minimize the levels of Mn in water supply sources prior to treatment and distribution. If such strategies are not used, or if Mn levels following such strategies remain greater than desired, treatment processes must be implemented to control the undesirable consequences of Mn in treated drinking water. Control of these impacts is most effectively achieved by removal to reach very low (e.g., < 0.015 to 0.020 mg/L Mn) levels in treated waters. In some cases, mitigation of some undesirable consequences can be achieved by the process of sequestration of Mn, which masks the impacts of Mn rather than removing Mn. The purpose of this chapter is to describe several treatment technologies for Mn control, beginning with an overview, then describing various technologies ending with consideration of the integration of Mn removal within overall water treatment objectives.

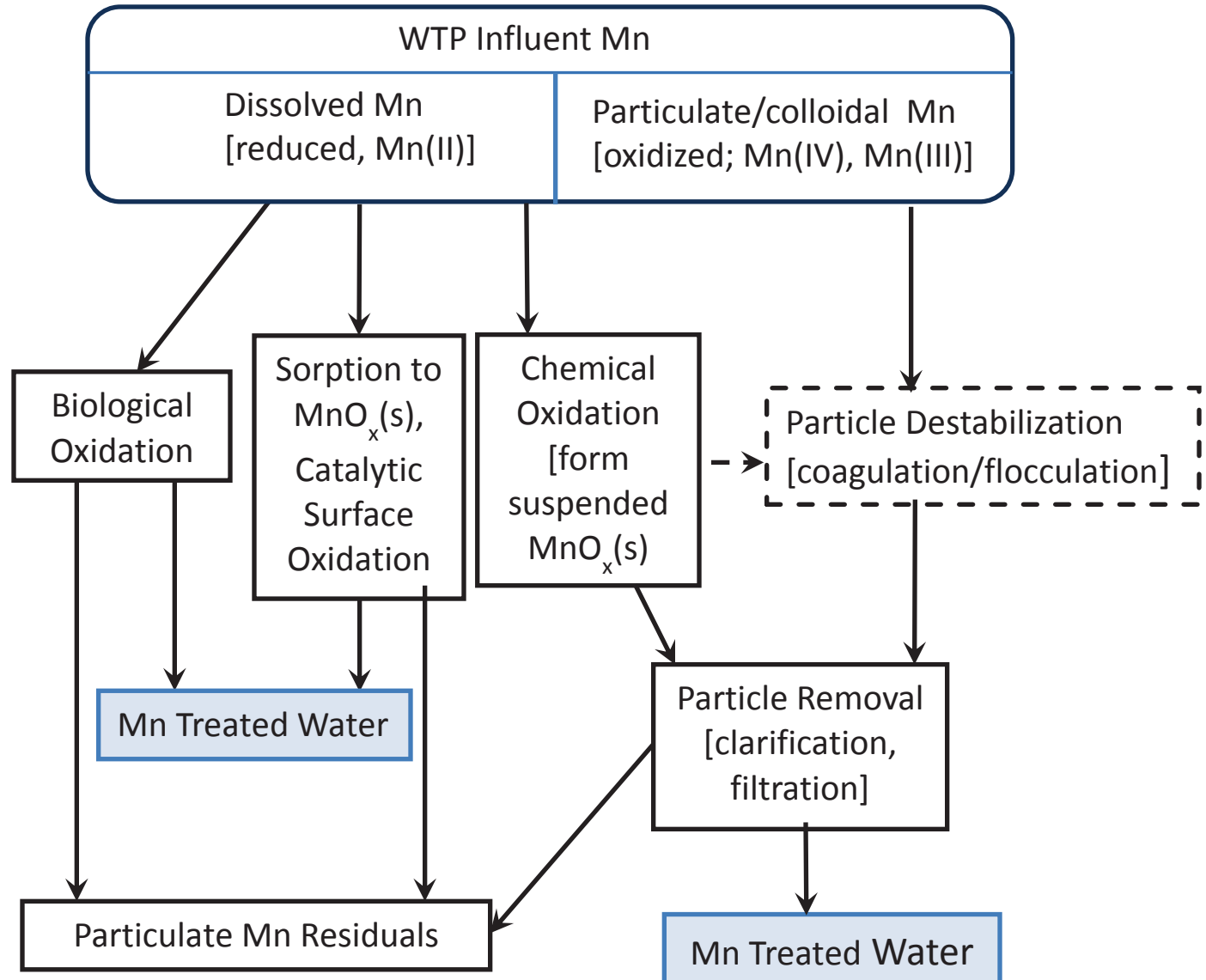
#### Characterization of Treatment Plant Influent Water Quality

A critical component for selection and operation of an effective Mn control process is to have appropriate knowledge of plant influent water quality. As described in detail in Chapters 3 and 4, critical information for Mn includes temporal data for both the concentration and the form of Mn. For some sources, such as a groundwater well, there may be very limited daily, seasonal or annual variability in Mn levels and all the Mn may be in the dissolved, reduced (Mn(II)) form. In contrast, a lake or reservoir source may experience very large seasonal variability in Mn levels; further, the Mn may occur in a variable distribution of dissolved, colloidal and particulate forms. Selection and operation of a treatment process very much depends on the level and form of Mn arriving at the treatment facility. Other influent water quality characteristics that can significantly influence process selection and performance include pH, temperature, alkalinity, hardness, natural organic matter (e.g. as measured by TOC), iron, reduced sulfur, nitrogen species, DO and other specific contaminants (e.g., arsenic, nitrate, etc.).

#### Removal of Mn

A schematic overview of Mn removal processes is shown in [Figure 6.1](#), beginning with the form of influent water Mn. Sometimes, although not commonly, influent water Mn is primarily in the particulate/colloidal form; one example is a run of river source. Often, however, a substantial fraction of the source water Mn is in the reduced, dissolved Mn(II) form. One approach for removal is to oxidize the Mn(II) to Mn(IV) (or Mn(III)), resulting in formation of  $\text{MnO}_x(\text{s})$  particles/colloids, followed by an appropriate solid/liquid separation process; possibilities include clarification by sedimentation or dissolved air flotation, media filtration and low pressure membrane filtration (microfiltration (MF) or ultrafiltration (UF)). Required treatment prior to solid/liquid separation depends on overall water quality, the form of  $\text{MnO}_x(\text{s})$  (colloidal or particulate), the intended removal process and the overall treatment train. For example, coagulation for particle destabilization and conversion of dissolved natural organic

matter (NOM) to particulate form and flocculation for particle aggregation, are typical ahead of clarification and media filtration for surface waters; particulate and aggregated colloidal Mn are effectively removed along with other particles. In contrast, a groundwater with reduced Mn(II) may be treated with a strong oxidant, creating particulate/colloidal Mn that can be removed directly using micro- or ultrafiltration membranes.



**Figure 6.1 Primary manganese removal approaches**

Another approach shown in Figure 6.1 is the sorption and catalytic oxidation treatment method. Granular media with  $\text{MnO}_x(\text{s})$ , either as a surface coating or throughout the media grain, can adsorb reduced Mn(II), which can then be readily oxidized on the surface, typically by free chlorine. This has traditionally been described as greensand filtration but the fundamental process has a much wider and more universal application as described later in this chapter. Surface oxidized Mn remains as a fixed coating or is removed by backwashing; in this sense, Mn removal from the process water is ultimately in particulate form.

Figure 6.1 also shows that reduced, dissolved Mn(II) can be removed by a biological process. Microorganisms supported by a granular medium take up and oxidize Mn(II); the resulting oxidized Mn is removed by backwashing of the granular media. Uptake of Mn(II) by  $\text{MnO}_x(\text{s})$  surfaces created by biological oxidation may also contribute to Mn removal.

An additional (although not typically used at the municipal level) method for removal of dissolved Mn is through use of an ion exchange (IX) process using cationic exchange media. The  $\text{Mn}^{2+}$  cation can be exchanged for  $\text{Na}^+$  or  $\text{H}^+$ ; ultimate removal is as  $\text{Mn}^{2+}$  in the salt brine used to regenerate the ion exchange media. This approach is not likely to be selected for Mn removal alone (except at the point of entry or point of use level); use of ion exchange for hardness removal, for example, would also result in removal of dissolved Mn.

## Sequestration

An alternative, lower treatment cost, approach to mitigating the negative impacts of supplying treated water with undesired levels of reduced Mn is known as sequestration. This process involves addition of a sequestering agent (usually a polyphosphate, possibly a silicate) in order to interact with Mn(II) to prevent oxidation, or formation of particles, during distribution and storage or upon use by the consumer. Removal of Mn is not achieved, so the approach is limited to relatively low levels of source water reduced metals (iron plus Mn). Preventing oxidation is challenging in systems with treated water pH and oxidant (e.g., free chlorine, oxygen) levels warranted by other water quality goals (e.g., microbial quality, lead and copper concerns, etc.).

## CHEMICAL OXIDATION AND PARTICLE REMOVAL

Chapter 2 of this manual describes the various valence states that may exist for Mn in water, ranging from the dissolved, reduced Mn(II) state to the highly oxidized, also dissolved, Mn(VII) state in the permanganate species. Within the typical realm of pH values present in anoxic (void of DO) groundwaters, Mn(II) predominates as the dissolved species of interest, able to be present at very high dissolved concentrations ( $>> 1 \text{ mg/L}$ ) over a wide range of pH conditions, until the potential for manganous carbonate ( $\text{MnCO}_3(\text{s})$ ) occurs, e.g., perhaps at pH values of 8- 9 or higher depending upon alkalinity levels. In oxygen-containing surface waters, dissolved Mn(II) is theoretically a stable species under acidic conditions (e.g., pH less than 5-6) but equilibrium forms of Mn under more alkaline pH values are the Mn(III) and Mn(IV) oxides ( $\text{MnO}_x(\text{s})$  solids – see Figure 2.1).

Thus, for WTP influents with dissolved Mn, a primary option utilized in water treatment practice is to: 1) dose one or more chemical oxidants to promote the direct chemical oxidation of Mn(II) into insoluble Mn(III) or Mn(IV) phases and, 2) use solid-liquid separation techniques subsequently to remove the  $\text{MnO}_x(\text{s})$  precipitates. This section of Chapter 6 describes key aspects of the chemical oxidation and particle removal processes used to achieve effective Mn removal.



## Chemical Oxidation: General Features

A few general comments are relevant when considering the effectiveness of any chemical oxidant for dissolved Mn(II) oxidation.

### *Oxidant Selection*

Chemicals that can effectively oxidize dissolved Mn(II) include potassium (or sodium) permanganate, chlorine dioxide, ozone, chlorine and oxygen. As described below for each of these specific oxidants, effectiveness depends on several factors, most notably pH, competing reactants and reaction time. Additionally, there are particular aspects of each specific oxidant that can affect chemical selection. For the pH range of approximately 6.5 to 8.5 and for reaction times within most treatment plants (minutes to a few hours), direct oxidation of dissolved Mn(II) is accomplished using one or more of the first three strong oxidants: permanganate, chlorine dioxide or ozone. At high pH (e.g., > 9 to 9.5), oxidation using chlorine or oxygen can occur; one example of this is Mn(II) oxidation during chemical softening of hard waters.

### *Dosing*

The required amount of chemical oxidant to dose depends on the stoichiometry of the reaction between the oxidant and Mn(II) as well as the stoichiometry of the reaction of the oxidant with all competing reactants, i.e., the overall oxidant demand. Chemical formulae showing the reactions of the five oxidants with Mn(II), including the theoretical stoichiometry of the oxidant requirements, are contained in [Table 6.1](#).

**Table 6.1**  
**Reactions of Mn(II) with several oxidants and the associated reaction stoichiometry**

Oxidant	Reaction	Stoichiometry
O <sub>2</sub> (aq)	$\text{Mn}^{2+} + 1/2\text{O}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}^+$	0.29 mg O <sub>2</sub> / mg Mn
O <sub>3</sub>	$\text{Mn}^{2+} + \text{O}_3(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + \text{O}_2(\text{aq}) + 2\text{H}^+$	0.87 mg O <sub>3</sub> /mg Mn
HOCl	$\text{Mn}^{2+} + \text{HOCl} + \text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + \text{Cl}^- + 3\text{H}^+$	1.30 mg HOCl as Cl <sub>2</sub> /mg Mn
ClO <sub>2</sub>	$\text{Mn}^{2+} + 2\text{ClO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 2\text{ClO}_2^- + 4\text{H}^+$	2.45 mg ClO <sub>2</sub> /mg Mn
KMnO <sub>4</sub>	$3\text{Mn}^{2+} + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(\text{s}) + 2\text{K}^+ + 4\text{H}^+$	1.92 mg KMnO <sub>4</sub> /mg Mn

A critical issue when considering the effectiveness of any chemical oxidant is that of competitive demands for the oxidant from other constituents in the water. Key among these is dissolved ferrous (Fe(II)) iron since each chemical oxidant considered for Mn(II) oxidation within water treatment facilities reacts much more rapidly with Fe(II) than with Mn(II). Hence, dosing intended for Mn(II) oxidation must be increased to account for Fe(II) present in the raw water. As an alternative, certain chemical oxidants (e.g., O<sub>2</sub>(aq) and/or free chlorine) could be added first to oxidize Fe(II) (since neither is particularly effective for Mn(II) oxidation but highly effective for Fe(II) oxidation), thereby decreasing the demand (dose) for a subsequent chemical that is effective for Mn(II) oxidation. Dissolved organic carbon (DOC) can likewise exert a

significant competitive demand for several of the oxidants available for Mn(II) oxidation, most notably when considering permanganate, chlorine dioxide or ozone as the oxidant of choice. Finally, groundwaters may contain reduced sulfur species and/or ammonia nitrogen and these can create competitive demands for certain chemical oxidants.

Dosing of a specific oxidant may be constrained or controlled by undesired by-products of the oxidant or unacceptable impacts of improper dosing. Examples, as described in more detail elsewhere, include the by-product chlorite anion ( $\text{ClO}_2^-$ ) from chlorine dioxide, “pink water” from excessive ozonation or permanganate dosing and halogenated disinfection byproducts (DBPs) from free chlorine. Thus, oxidant selection, dosing and raw water quality are interrelated and must be jointly considered.

### ***Reaction Kinetics***

In addition to selecting the type and dose of oxidant, process designers must consider the time required for extensive Mn(II) oxidation. The rate of Mn(II) oxidation is affected by several factors including temperature, pH and concentrations of oxidant and reduced Mn.

Solution temperature can have a significant effect on the kinetics of interaction between any oxidant and Mn(II), with slower reaction kinetics occurring at lower temperatures. Fortunately, temperature often does not have a major impact on Mn(II) oxidation in most treatment situations. In groundwater treatment the water temperature is typically at least at 10°C or higher, so extreme kinetic impacts from lower temperatures are not observed. Surface water sources can have much lower temperatures in the winter months (e.g., 0.5 to 4°C). Fortunately, elevated dissolved Mn(II) levels in surface waters are most prevalent in the summer and early fall months such that chemical oxidants are typically used under water temperatures of 10°C as a minimum, with values often well above 20°C.

One of the most important factors that affects the rate of Mn(II) oxidation is the water pH. In general, oxidation rates increase as pH increases, but the relative impact of pH varies greatly between oxidants. Research studies have shown that the rate of oxidation of Mn(II) by strong oxidants such as permanganate, chlorine dioxide and ozone is significantly increased as pH is increased from 5 or 6 to 7 or 8 (Knocke et al., 1991b; Reckhow et al., 1991), yet required reaction times are very short even at the lower pH (e.g., less than one minute). Practical experience indicates that reaction times of at least a few minutes for permanganate oxidation of Mn(II) should be provided and that increasing pH to 7 to 7.5 significantly improves oxidation performance compared to pH of 6 to 6.5. Reaction rates for ozone and chlorine dioxide are typically so rapid for most source water pH conditions that increasing pH for improved Mn(II) oxidation alone may not be warranted.

For free chlorine and oxygen, pH has a very significant and important impact on the rate of Mn(II) oxidation. In the typical pH range of 6 to 8 for many water treatment facilities, the rate of direct Mn(II) oxidation by DO or free chlorine is too slow to be of importance in the timeframe of the treatment plant. However, if pH is increased significantly, the rate of Mn(II) oxidation can increase such that oxidation and precipitation of Mn by free chlorine or oxygen can occur within minutes (or less). One example is a surface water treatment plant in the US northeast that applies lime and chlorine after sedimentation but prior to media filtration, resulting in a pH of 9.5 to 10 and rapid oxidation of seasonally occurring dissolved Mn prior to the filters.

Another example, as noted above, is oxidation by oxygen in conjunction with the high pH used in chemical softening by lime or lime/soda addition.

### ***Reaction Time and Location of Oxidant Addition***

The reaction time needed or provided for chemical oxidation of Mn(II) depends on several factors including the specific oxidant and other treatment objectives. Two important aspects for permanganate addition are that 1) it is not used for disinfection purposes and, 2) the Mn(VII) in permanganate is reduced to Mn(IV) by oxidation of Mn(II) (and other reduced species), thus creating additional  $\text{MnO}_x(\text{s})$  particles. These factors dictate that reaction time be provided explicitly for Mn(II) oxidation and that additional attention be provided to prevent overdosing of permanganate. Dosing of permanganate to WTP influent is most common; reaction time can be provided in piping between a reservoir or pump station source and the WTP or it can be provided in reactors specifically constructed for this purpose. Using a pipeline reactor has the advantage of nearly plug flow reactor hydraulics, excellent for maximizing oxidation of Mn(II) and avoiding construction of an additional reactor. Reactors constructed explicitly for Mn(II) oxidation should be designed to minimize short-circuiting; using baffled tanks or tanks-in-series is recommended. For relatively soft surface waters that use hydrolyzing metal salt coagulants, providing for base addition to increase pH prior to permanganate addition is beneficial for both increasing the rate of Mn(II) oxidation and maintaining a desired minimum pH after coagulant addition.

For strong oxidants that are also disinfectants, such as chlorine dioxide and ozone, the reaction time provided may be controlled by design to achieve a specified level of disinfection (e.g., CT for X log *Giardia* inactivation) and may greatly exceed the time needed for Mn(II) oxidation. However, it is often desirable to apply disinfectants at an intermediate stage after removal of significant disinfectant demand (and DBP precursors) by coagulation, flocculation and clarification but prior to filtration. The  $\text{MnO}_x(\text{s})$  particles created by oxidation of Mn(II) during intermediate disinfection/oxidation will most likely need to be destabilized by coagulant addition for effective removal in granular media filters; low pressure, typically hollow fiber, MF or UF membrane filters would not require particle destabilization prior to filtration.

### ***Determining Oxidation Effectiveness - Bench-Scale Testing & Measurements***

Because the stoichiometry and rate of direct chemical oxidation reaction are not dependent on the hydraulics of treatment plants, bench-scale laboratory testing can be used to assess the effectiveness of different oxidants and the associated dosing and reaction time requirements. Oxidants and pH control chemicals should be applied to a batch reactor (a jar or beaker) in the expected full-scale sequence and to the appropriate water to be treated (e.g., raw versus clarified). Samples should be taken after specified relevant reaction times for fractionation of Mn. At a minimum, total and filtered levels should be determined, allowing for assessment of formation of particulate Mn; further fractionation by membrane ultrafiltration to distinguish between dissolved and colloidal fractions may also be needed, especially for effluents from intermediate oxidation reactors. Samples must be fractionated at the time of collection as

additional oxidation may occur, leading to over estimation of the actual extent of oxidation at the point of sampling.

As noted elsewhere, sampling across a treatment plant and fractionation of Mn into its different forms provides “the facts” regarding Mn levels and its transformation. Measurement of conversion of dissolved Mn in raw water to particulate or colloidal form after oxidant addition and reaction time indicates oxidation effectiveness. Similarly, measurement of loss of solid phase Mn following clarification/filtration processes demonstrates effective removal of particles. Measurement of only total manganese in a filter effluent is not informative as one does not know if, for example, elevated Mn is due to poor particle removal or lack of pre-filter oxidation effectiveness.

### **Effectiveness of Specific Chemical Oxidants**

Each of the potential oxidants for conversion of Mn(II) to Mn(IV) has specific characteristics of importance. [Table 6.2](#) summarizes oxidant characteristics and the following paragraphs describe each oxidant in detail.



**Table 6.2**  
**Summary of chemical oxidants**

Oxidant name	Chemical formula	pH and rxn rate	Direct oxidation aspects
Permanganate (purchase as potassium or sodium salt)	$\text{MnO}_4^-$	Fast at pH > ~6 (2 to 4 minutes)	<ul style="list-style-type: none"> <li>- Overdose causes pink water</li> <li>- Adds Mn to water</li> <li>- Possible taste &amp; odor benefits</li> <li>- Forms colloidal <math>\text{MnO}_x(\text{s})</math></li> </ul>
Chlorine Dioxide	$\text{ClO}_2(\text{aq})$	Fast, little pH impact (1 to 2 minutes)	<ul style="list-style-type: none"> <li>- Generate on-site</li> <li>- Dosing limited by chlorite DBP MCL</li> <li>- Forms colloidal <math>\text{MnO}_x(\text{s})</math></li> </ul>
Ozone	$\text{O}_3(\text{aq})$	Fast, little pH impact (1 to few minutes)	<ul style="list-style-type: none"> <li>- Generate on-site</li> <li>- Overdose can create pink water</li> <li>- Hard to yield <math>\text{Mn}_{\text{diss}} &lt; 20 \mu\text{g/L}</math></li> <li>- Forms colloidal <math>\text{MnO}_x(\text{s})</math></li> </ul>
Free Chlorine	$\text{HOCl}$ , $\text{OCl}^-$	Slow until pH > 8 to 9.	<ul style="list-style-type: none"> <li>- Not effective for direct oxidation at pH &lt; 8 – 9</li> <li>- Very effective for surface oxidation</li> </ul>
Oxygen	$\text{O}_2(\text{aq})$	Very slow until pH > 9 – 9.5	- Only significant in high pH softening
Hydrogen Peroxide	$\text{H}_2\text{O}_2$	NOT EFFECTIVE for Mn(II) Oxidation	

### ***Potassium and Sodium Permanganate***

Potassium permanganate ( $\text{KMnO}_4$ ) has been traditionally used for decades as a chemical for oxidation of dissolved Mn(II) in water treatment operations. The theoretical dosage required to oxidize Mn(II) to insoluble Mn(IV) species is 1.9 mg  $\text{KMnO}_4$  per mg Mn(II); however, competitive oxidant demand from other constituents such as solution DOC can significantly increase the overall dosage requirement. The kinetics of interaction between  $\text{KMnO}_4$  and Mn(II) are fairly rapid, especially for pH conditions at or above 6.0. Reaction times of 2 to 4 minutes may be necessary for lower initial Mn(II) concentrations and/or lower pH values, whereas shorter reactions times may be required for high pH conditions due to more rapid reaction kinetics. Studies have indicated that the by-product  $\text{MnO}_x(\text{s})$  formed can be colloidal in nature, with particle sizes well below one micron. As such, it is important whenever possible to add  $\text{KMnO}_4$  upstream of coagulation/flocculation processes so that these colloidal materials may be destabilized and appropriately aggregated for subsequent solid-liquid separation. Many utilities will use some portion of the raw water supply line to the water treatment facility for providing this reaction time; for example, some water utilities will practice  $\text{KMnO}_4$  addition near the raw water pumping station and allow the detention time for transport to the treatment plant to yield effective Mn(II) oxidation.

Appropriate dosing of  $\text{KMnO}_4$  is key to overall process effectiveness, as underdosing results in elevated dissolved Mn(II) concentrations in the finished water and overdosing can

result in the production of “pink water” due to the presence of unreacted  $\text{KMnO}_4$  in the finished water. Pink water situations must be avoided as release of unreacted  $\text{KMnO}_4$  in the finished water will lead to  $\text{MnO}_x(\text{s})$  precipitation in the distribution system, resulting in increased water turbidities as well as consumer complaints due to water discoloration.

Potassium permanganate is typically purchased in dry form (95 to 99% purity) and then dissolved onsite into a concentrated solution that is fed at the appropriate dosing point in the water treatment train by a metered pump. Storage of dry  $\text{KMnO}_4$  requires low moisture conditions to avoid “caking” of the material and more challenges in its mixing and dissolution. Typical  $\text{KMnO}_4$  feed solutions are prepared in concentrations of 1-5 % by dry weight. Water utilities at times note difficulties with respect to the dissolution of solid  $\text{KMnO}_4$  in the preparation of these feed solutions. Also, the use of  $\text{KMnO}_4$  does require the handling of the dry stock material coupled with equipment for achieving dissolution of the solid  $\text{KMnO}_4$  into the concentrated feed solution.

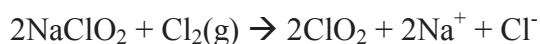
*Cleaning Solution for  $\text{KMnO}_4$  Stains*

- 15 mL peroxide
- 20 mL vinegar
- 15 mL water

A large number of utilities in recent years have switched to the use of sodium permanganate ( $\text{NaMnO}_4$ ) as this chemical form of permanganate has far greater solubility in water, allowing for concentrated (e.g., 20 or 40% by weight) solutions to be prepared. These highly concentrated solutions can thus be prepared at the manufacturer and shipped to the water treatment facility, eliminating the need for equipment at the facility for dissolution of the dry product. Sodium permanganate handling and feed systems can thus be far less costly from a capital equipment standpoint. However, the bulk chemical costs of sodium permanganate (expressed on an equivalent weight  $\text{MnO}_4$  basis) are often much greater than potassium permanganate. The stoichiometric requirement to oxidize 1 mg/L of  $\text{Mn(II)}$  to insoluble  $\text{Mn(IV)}$  is approximately 1.7 mg  $\text{NaMnO}_4$  per mg  $\text{Mn(II)}$ . The 40% by weight solution is considered to be substantially more aggressive than the 20% solution, leading to reports at some utilities of leaks in certain aspects of the piping and feed system. Care should be exercised in the design of either type of chemical feed system to ensure capability of the materials with the chemical solution.

### ***Chlorine Dioxide***

Chlorine dioxide ( $\text{ClO}_2$ ) is a very strong oxidant that has been demonstrated to be quite effective at promoting dissolved  $\text{Mn(II)}$  oxidation. Onsite generation of  $\text{ClO}_2$  is required due to its high degree of reactivity and relative instability in water. Probably the most common method of generating  $\text{ClO}_2$  is through reaction of either  $\text{HOCl}$  or gaseous chlorine ( $\text{Cl}_2$ ) with sodium chlorite, as shown below:



These reactions optimize  $\text{ClO}_2$  formation in the pH range from 3.5 to 5.5, with lower pH values leading to greater production of the by-product chlorate ( $\text{ClO}_3^-$ ), which is an undesirable

outcome given health related concerns associated with unregulated levels of chlorate in drinking water. In the case of the reaction with HOCl it is often necessary to add acid to the reaction to neutralize the basicity generated, thereby allowing the pH to remain in the desired acidic range stated. Chlorine dioxide can also be generated by exposing sodium chlorite to a strongly acidic environment:



The stability of  $\text{ClO}_2$  is decreased at elevated temperatures, alkaline pH conditions and/or by the presence of light. Each of these situations can enhance the disproportionation of the compound into chlorite and chlorate.

While  $\text{ClO}_2$  theoretically can accept up to five electrons in an oxidation-reduction reaction (being fully reduced to chloride ( $\text{Cl}^-$ )) its chemical interaction with dissolved  $\text{Mn(II)}$  yields  $\text{ClO}_2^-$  (chlorite) as the by-product, which represents only a net acceptance of one electron. As a result, little of the overall oxidizing capacity of the  $\text{ClO}_2$  is realized when reacting with  $\text{Mn(II)}$ . This results in the theoretical stoichiometry of interaction being 2.45 mg  $\text{ClO}_2$  per mg  $\text{Mn(II)}$  being oxidized. Further, this interaction produces residual  $\text{ClO}_2^-$  which is limited in drinking water to no more than 1.0 mg/L (chlorite MCL). Also,  $\text{ClO}_2$  reacts fairly rapidly with DOC in water, creating a significant competitive oxidant demand; likewise, the interaction with DOC typically results in approximately 65 to 75% of the applied  $\text{ClO}_2$  remaining as residual  $\text{ClO}_2^-$ . Legal limits on  $\text{ClO}_2^-$  concentrations in drinking water effectively limit the amount of  $\text{ClO}_2$  that can be added to water to approximately 1.4 mg/L or less. One technique available for removing  $\text{ClO}_2^-$  from drinking water is to add ferrous ( $\text{Fe(II)}$ ) iron to the water. This oxidation-reduction reaction converts the  $\text{ClO}_2^-$  to residual  $\text{Cl}^-$ , with the iron being converted to ferric ( $\text{Fe(III)}$ ) iron, which would subsequently precipitate as  $\text{Fe(OH)}_3(\text{s})$ . Depending upon the location of this ferrous iron addition, the by-product  $\text{Fe(OH)}_3(\text{s})$  could enhance the coagulation/flocculation processes within the treatment plant.

Reaction kinetics between  $\text{ClO}_2$  and dissolved  $\text{Mn(II)}$  are rapid, with required typical reaction times of 1 to 2 minutes or less, depending upon the dosage of  $\text{ClO}_2$  employed as well as the initial dissolved  $\text{Mn(II)}$  concentration. As with permanganate oxidation, the interaction between  $\text{ClO}_2$  and dissolved  $\text{Mn(II)}$  can produce colloidal-size  $\text{MnO}_x(\text{s})$  solids, especially in waters of relatively low hardness. This leads to beneficial application of  $\text{ClO}_2$  for  $\text{Mn(II)}$  oxidation in the raw water line to the water treatment facility; some utilities have built a small basin upstream of the rapid mix basin to likewise provide a nominal amount of detention time for promoting the reaction between  $\text{ClO}_2$  and dissolved  $\text{Mn(II)}$  (discussed as part of the Fort Collins case study in Chapter 7). The goal is to yield formation of the by-product  $\text{MnO}_x(\text{s})$  solids prior to coagulation/flocculation processes to promote destabilization of these colloidal solids and their aggregation into the flocs being formed prior to solid-liquid separation processes later in treatment.

Of the chemical oxidants available,  $\text{ClO}_2$  probably can produce the lowest residual dissolved  $\text{Mn(II)}$  concentrations in the finished water. Overdosing of  $\text{ClO}_2$  does not result in permanganate formation whereas overdosing of either permanganate or ozone for  $\text{Mn(II)}$  can yield residual permanganate (pink water) conditions. However, limitations on residual  $\text{ClO}_2^-$  coupled with competitive DOC demands can make the oxidation of dissolved  $\text{Mn(II)}$  challenging

to complete with  $\text{ClO}_2$  addition alone. In such situations, treatment plants have employed a combination of permanganate addition with  $\text{ClO}_2$  addition to achieve overall  $\text{Mn(II)}$  removal.

One final point of concern regarding  $\text{ClO}_2$  is that the residual  $\text{ClO}_2^-$  present can react with free chlorine (added for residual disinfectant in the water distribution system) to regenerate  $\text{ClO}_2$  which, being volatile, can be released in the consumer's home and yield various types of odor complaints.

### ***Ozone***

Ozone ( $\text{O}_3$ ) is the strongest chemical oxidant routinely employed at water treatment facilities. It is formed by the passage of either an air or gaseous oxygen stream across a corona discharge field, producing a by-product stream containing  $\text{O}_3$ . The high reactivity and instability of  $\text{O}_3$  necessitates its production at the water treatment facility. A primary cost factor in its generation is that of electrical power. Also, all off-gas sidestreams generated as a result of feeding  $\text{O}_3$  must be treated prior to release to the atmosphere. Human health and safety considerations regarding exposure to  $\text{O}_3$  require enclosing all basins where  $\text{O}_3$  is fed into water to minimize exposure to  $\text{O}_3$ .

The chemistry of  $\text{O}_3$  in water is highly complex, with many pathways involved in how it reacts with dissolved species in solution. The primary oxidative species of interest in drinking water applications are molecular  $\text{O}_3$  and the uncharged hydroxyl radical  $\text{OH}$ . The  $\text{OH}$  radical is often the predominant oxidative species present in waters dosed with  $\text{O}_3$  when the solution pH is more acidic and/or, more importantly, the alkalinity of the water is reduced. Conversely, waters of higher alkalinity tend to have lower amounts of the  $\text{OH}$  radical present as the inorganic bicarbonate and carbonate ions tend to react with the radical and neutralize its oxidative effectiveness. In these waters more of the oxidative power of the ozone remains in the molecular  $\text{O}_3$  form.

Research studies have indicated that it is the molecular  $\text{O}_3$  species that actually oxidizes dissolved  $\text{Mn(II)}$  in water; further, that the  $\text{OH}$  radical is relatively ineffective at  $\text{Mn(II)}$  oxidation. The stoichiometric requirement for  $\text{Mn(II)}$  oxidation is 0.87 mg  $\text{O}_3$  per mg  $\text{Mn(II)}$ . The actual dosage required for effective  $\text{Mn(II)}$  oxidation will vary as the alkalinity of the water changes, with higher dosages being required in lower alkalinity waters to account for the conversion of much of the applied  $\text{O}_3$  to the  $\text{OH}$  radical. The presence of DOC in solution can likewise create a substantial competitive  $\text{O}_3$  demand when considering  $\text{Mn(II)}$  oxidation. As a result the attempt to use  $\text{O}_3$  for dissolved  $\text{Mn(II)}$  oxidation in organic-laden, low alkalinity surface waters can yield required  $\text{O}_3$  dosages several times above that of the stoichiometric requirement.

The kinetics of  $\text{Mn(II)}$  oxidation by  $\text{O}_3$  are similar to those observed with permanganate and chlorine dioxide under similar conditions of solution pH and temperature. In general, reaction times of less than one to several minutes may be required, with more rapid kinetics observed at higher initial  $\text{Mn(II)}$  and/or  $\text{O}_3$  concentrations. One difference with  $\text{O}_3$  oxidation of dissolved  $\text{Mn(II)}$  is that the minimum residual dissolved Mn concentration achieved is often at or above 20 to 25  $\mu\text{g/L}$ , whereas oxidation with either permanganate or chlorine dioxide can often yield residual dissolved Mn concentrations at or below 10  $\mu\text{g/L}$ . The reason for this more elevated residual dissolved Mn concentration is unclear, but from a practical standpoint  $\text{O}_3$



addition alone is unable to achieve the 15 µg/L residual Mn concentrations that a water utility may desire to minimize water discoloration complaints from consumers due to chronic buildup of Mn in the distribution system.

Finding the appropriate O<sub>3</sub> dosage to minimize the residual dissolved Mn concentration can be difficult. As noted previously, competitive oxidant demands often create a need for O<sub>3</sub> dosages to be well above the stoichiometric requirement for Mn(II) oxidation. Also, O<sub>3</sub> has the ability to oxidize insoluble Mn(III) and Mn(IV) species to the Mn(VII) valence state of permanganate. Thus, excess O<sub>3</sub> dosing for Mn(II) oxidation has the potential to yield permanganate generation, resulting in “pink water”. If any residual permanganate were to leave the water treatment facility it could subsequently react as an oxidizing agent and yield by-product MnO<sub>x</sub>(s) solids, which could in turn lead to consumer complaints of water discoloration.

The oxidation of dissolved Mn(II) by O<sub>3</sub> often yields colloidal-size MnO<sub>x</sub>(s) solids that are difficult to settle and/or filter from the water. This colloidal formation is especially noticeable in waters of lower hardness. While this is similar to what happens when Mn(II) is oxidized by permanganate or chlorine dioxide, a major difference is that these two oxidants are often added prior to coagulant addition; thus, the colloidal MnO<sub>x</sub>(s) solids formed are aggregated into the flocs formed by coagulation and subsequent flocculation of the water. In contrast O<sub>3</sub> is often first added downstream of clarification so as to decrease the DOC of the water and, correspondingly, its O<sub>3</sub> demand. In that situation the dissolved Mn(II) would first be oxidized by the O<sub>3</sub> post-coagulant addition and sedimentation. The resulting colloidal MnO<sub>x</sub>(s) solids are also highly negatively charged under the pH conditions typical in water treatment facilities. The capture of these colloidal, negatively charged solids can be problematic within typical dual-media filters, allowing for the possible penetration of some amount of these MnO<sub>x</sub>(s) into the finished water. Many water utilities have found it necessary to add a small amount of either a polymer or a polyaluminum chloride coagulant downstream of the ozonation treatment stage to help destabilize and aggregate these MnO<sub>x</sub>(s) colloids.

The summation of these various issues associated with O<sub>3</sub> oxidation of dissolved Mn(II) has resulted in many water utilities being unable to rely solely on O<sub>3</sub> for effective Mn control. Instead, other strategies may need to be employed. For example Wilczak *et al.*, (1993) conducted extensive pilot-scale testing to optimize the usage of O<sub>3</sub> for water treatment usage. In this study, O<sub>3</sub> addition was desired for water disinfection, reductions of DBPs and dissolved Mn(II) control. After many months of pilot-scale testing, the authors concluded that wide variations in the O<sub>3</sub> demand of the water (primarily due to variations in the raw water DOC concentration) made it very difficult to concurrently achieve effective Mn control. As a result the authors concluded that the use of potassium permanganate as a pre-oxidant was the most effective means of insuring low residual dissolved Mn concentrations in the treated water.

### ***Dissolved Oxygen***

Molecular oxygen ( $O_2(aq)$ ) can theoretically oxidize dissolved Mn(II) over most pH conditions associated with natural waters or that would be present in water treatment operations. However, the kinetics of this oxidation reaction are extremely slow unless the pH of the water is at or above 9.0 to 9.5. Hence,  $O_2(aq)$  is effective as a chemical oxidant of dissolved Mn(II) typically only when lime or lime-soda ash softening treatment methods are being employed. However, coupling the presence of  $O_2(aq)$  with Mn-oxidizing bacteria can produce very effective oxidation of dissolved Mn(II) over a much broader pH range (e.g., biological Mn oxidation has been reported to occur under water treatment conditions at pH values as low as 6.5). Discussion regarding biological methods of Mn oxidation and the role of  $O_2(aq)$  in such systems is presented later in this chapter.

Oxidation of Mn(II) by  $O_2(aq)$  in lime or lime-soda ash softening of groundwaters typically requires the direct addition of oxygen to the water, which can be accomplished by either packed tower or tray aeration facilities to promote  $O_2(g)$  transfer into the liquid phase. (In practice aeration may also be required to meet other treatment objectives such as  $CO_2$  stripping, Fe oxidation, or  $H_2S$  stripping which are common for groundwater.) On the other hand, surface waters typically contain more than sufficient quantities of  $O_2(aq)$ , so further addition of oxygen is unnecessary. Instead, the only requirement for initiating this oxidation reaction is the lime or lime-soda ash addition to generate pH conditions of 9.5 or higher (which is characteristic of this softening process).

### ***Free Chlorine (Hypochlorous Acid/Hypochlorite)***

Free chlorine (denoting either the hypochlorous ( $HOCl$ ) species or the hypochlorite ion ( $OCl^-$ ) is thermodynamically unstable with respect to reduced Mn(II), meaning it theoretically can oxidize Mn(II) to either insoluble Mn(III) or Mn(IV) oxide species across the entire pH range of interest in water treatment situations. However, kinetics once again play a key role in defining the overall effectiveness of free chlorine for dissolved Mn(II) oxidation. Slow reaction kinetics prevail unless the solution pH is typically at or above 8.0, at least in terms of promoting effective Mn(II) oxidation within the time scales employed within water treatment facilities. [Table 6.1](#) shows a theoretical stoichiometry of interaction of 1.3 mg free chlorine (as  $Cl_2$ ) for each mg of reduced Mn(II) being oxidized. However, given the slow reaction kinetics at typical treatment pHs and competing chlorine demand, the actual dosage of free chlorine required to promote significant Mn(II) oxidation may be many times higher than this theoretical stoichiometry.

While free chlorine is relatively ineffective at promoting Mn(II) oxidation within the time scale of typical water treatment facilities, it can promote significant amounts of Mn(II) oxidation within water distribution systems due to the longer detention times prevalent (typically several days, including water system storage and piping). As a result, having elevated dissolved Mn(II) levels in the finished water of a treatment plant coupled with maintenance of a free chlorine residual in the water distribution system can yield significant Mn(II) oxidation and resulting consumer complaints related to water discoloration. A Water Research Foundation report (Kohl and Medlar 2006) demonstrated significant decreases in dissolved Mn(II) concentrations in water distribution systems employing free chlorine residuals as the water traveled further from the

water treatment plant. The resulting oxidized Mn particulates may settle in water pipes, become attached to pipewall deposits and/or continue directly to the consumer's tap. Each of these outcomes increases the potential for water quality complaints from consumers.

The subsequent section of this chapter on the use of Mn greensand and/or standard filter media that has an  $\text{MnO}_x(\text{s})$  surface coating demonstrate the key role that free chlorine has in promoting effective dissolved Mn(II) removal in these systems. Hence, free chlorine can be an effective part of an overall strategy for achieving Mn removal within a water treatment facility. However, it must be employed at the right stage of treatment (typically in conjunction with Mn greensand or  $\text{MnO}_x(\text{s})$ -coated filter media) to be effective. As a bulk solution oxidant for Mn(II) removal it is relatively ineffective unless fairly alkaline pH conditions are being utilized.

### ***Hydrogen Peroxide***

The use of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in water treatment has increased over the past few decades, normally in conjunction with the addition of either  $\text{O}_3$  or ultraviolet (UV) light. These coupled additions yield very strong oxidizing conditions in water and are often referred to as “advanced oxidation processes or AOPs”. However,  $\text{H}_2\text{O}_2$  addition alone has not proved effective for dissolved Mn(II) oxidation. Further, literature sources evaluating  $\text{H}_2\text{O}_2$  use as an AOP with either  $\text{O}_3$  or UV light have not focused on the ability of such systems to promote effective Mn(II) oxidation. These AOPs are thought to achieve desired oxidation outcomes through the generation of significant amounts of the OH radical. Since the OH radical is felt to be relatively ineffective for promoting dissolved Mn(II) oxidation it appears unlikely that either of these AOPs would result in effective Mn(II) oxidation. As a result water treatment facilities that employ  $\text{H}_2\text{O}_2$  addition alone or as part of an AOP approach to treatment will most likely require another means of achieving Mn(II) oxidation in order to achieve desired finished water Mn concentrations.

### **Removal of Manganese Particles**

Direct chemical oxidation of dissolved Mn(II) creates particulate and colloidal  $\text{MnO}_x(\text{s})$  material that must be properly removed to achieve Mn treatment goals for finished water as well as low treated water turbidity. Mn particles can be removed by any process used for solid-liquid separation and may represent a minor contribution to the total mass of particulate matter removed or may be the majority of the particle mass removed during treatment. A key aspect of effective treatment is consideration of where in the treatment train the Mn particles are created. Several representative treatment scenarios are considered.

### ***Groundwater with only Mn as Primary Concern***

Some groundwater sources have relatively constant yet elevated levels of dissolved Mn(II) with low levels of other potential contaminants such as iron or DOC. For this type of water, direct chemical oxidation of Mn(II), often by dosing of permanganate, followed immediately by filtration for particle removal may be utilized. Media filters, perhaps comprised of a dual media of anthracite over greensand or other media, can be used to remove  $\text{MnO}_x(\text{s})$  particles. As noted elsewhere in this chapter, when permanganate is continuously applied ahead of media filtration, it is likely that much of the Mn removal is due to particle filtration in contrast to sorption of Mn(II) and catalytic surface oxidation. Mn oxide particles formed from both Mn(II) oxidation and Mn(VII) reduction can also be effectively removed by direct filtration using submerged or pressurized hollow fiber membrane filtration (i.e., MF or UF). Example facilities include those in Littleton, Seekonk and Hadley, Massachusetts. The solid residuals from treatment of this type of source are mostly Mn oxides, produced by backwashing/backflushing the media/membrane filters. Treated water recovery can be increased by recycling waste backwash water after particle removal by sedimentation (e.g., Seekonk, MA) or by a second stage of membranes (e.g., Hadley, MA and Littleton, MA). A process schematic for one facility is shown in [Figure 6.2](#).

### ***Groundwater with Mn and other Contaminants***

Groundwater sources with elevated levels of Mn(II) often have other constituents of concern, most notably reduced iron (Fe(II)) and possibly DOC, as well as hardness and other dissolved cations and anions (e.g., nitrate, sulfide, arsenate, etc.). The oxidant demand of Mn(II) as well as species other than Mn(II) must be satisfied by chemical dosing. Because Fe(II) is readily oxidized to Fe(III) by oxygen and free chlorine, it may be appropriate to first apply one of these oxidants and then apply a strong oxidant for Mn(II) oxidation either before or after removal of the iron hydroxide precipitate by clarification and filtration. If a strong oxidant is applied for Mn(II) oxidation after filtration for iron hydroxide removal, a second stage filtration step is needed for particle removal. Another option may be to use a second stage of appropriate media for Mn removal by sorption and surface oxidation with continuous addition of free chlorine ahead of the second stage. If the groundwater also contains elevated levels of DOC, removal of some organic matter in a first stage filter prior to a second stage catalytic surface oxidation process may be required to limit the formation of DBPs (see Aquarion case study in Chapter 7). The reduction of DOC concentrations and removal of DBP precursors may be accomplished by any of several techniques including enhanced coagulation, granular activated carbon, powered activated carbon, ion exchange or other methods.

### ***Surface Water with Pre-oxidation of Mn(II)***

Lake and reservoir surface water sources may have annual seasonal occurrence of elevated levels of raw water Mn (see case studies in this manual for examples). For such sources it is also common to utilize coagulation to convert DOC to particulate form and to destabilize raw water particles (measured as turbidity or algae, etc.) prior to flocculation for particle aggregation followed by either clarification and filtration, or by direct filtration. As such, it can



be effective to add, either only when needed or continuously, a strong oxidant such as permanganate or chlorine dioxide to the raw water to oxidize Mn(II) to particulate form prior to the coagulation/flocculation and particle removal processes. The Mn particles are incorporated into flocculated material and removed along with other particles and often represent a minor contribution to the mass of particles being removed (e.g., less than 1 or 2 mg/L of Mn oxide solids within 10's of mg/L of total suspended solids removed). The challenge for this approach is to achieve effective oxidant dosing during a potentially rapidly changing influent Mn concentration along with variable competing oxidant demands. A schematic of this type of process is shown in [Figure 6.3](#).

Informative results of fractionation of Mn across a surface water direct filtration plant that uses potassium permanganate pre-oxidation are shown in [Figure 6.4](#) (Tobiason and Vinod, 1992). These data show that the raw water had approximately 0.07 mg/L of Mn, mostly dissolved. The total Mn is of course increased by permanganate addition and much of the Mn is in the colloidal form after oxidant addition. However, the Mn is converted to particulate form after coagulant addition and rapid mixing such that media filtration results in a filter effluent level of 0.02 mg/L, all in dissolved form. Results for a parallel pilot study are also shown. Pre-oxidation with ozone also creates colloidal Mn but is less effective than permanganate. After rapid mixing, the colloidal particles following pre-ozonation are also converted to particulate form. Also shown are results for a pilot train with no pre-oxidation, illustrating the lack of Mn(II) oxidation without the pre-oxidant.

As noted in Chapter 3, “removed” Mn particles can become an unintended source of Mn if residuals with Mn oxides are not carefully managed. Sludge that accumulates in a sedimentation basin can release dissolved Mn(II) if reducing conditions develop while liquid stream recycle from processes for solids removal from clarification sludge and/or waste filter backwash can contain significant levels of Mn. Appropriate management of residuals is a critical component of overall treatment for Mn control. The reader is directed to the Newport News Water Authority case study (presented later in this manual) for representative information related to the levels of Mn that may be present in waters recycled from solids processing systems. Likewise, a novel application of  $\text{MnO}_x(\text{s})$ -coated filter media for removing dissolved Mn from these waters is also described.

### ***Surface Water with Intermediate Oxidation of Mn(II):***

As noted previously, it may be advantageous for disinfection and other purposes to apply a strong oxidant to waters after clarification (e.g., dissolved air flotation or sedimentation) but prior to filtration, often referred to as intermediate oxidation (or disinfection). Removal of NOM and particles can decrease the oxidant dose required to achieve a measurable residual for disinfection credit or other treatment goal. If dissolved Mn(II) enters the intermediate oxidation process, which will occur when Mn(II) is in the raw water, Mn oxide particles will be produced; a typical example is use of ozonation prior to biologically active media filtration. The  $\text{MnO}_x(\text{s})$  colloids/particles are likely to be stable due to negative surface charge and may not be removed completely by media filtration which requires destabilized influent particles for effective performance. As such, addition of a low dose of a pre-filter coagulant such as polyaluminum chloride (PACl) or cationic polymer may be required for removal of the Mn particles. A

schematic of this type of process is shown in Figure 6.5; an example of an intermediate ozonation facility (Newport News, VA) is presented in the case studies within this manual.

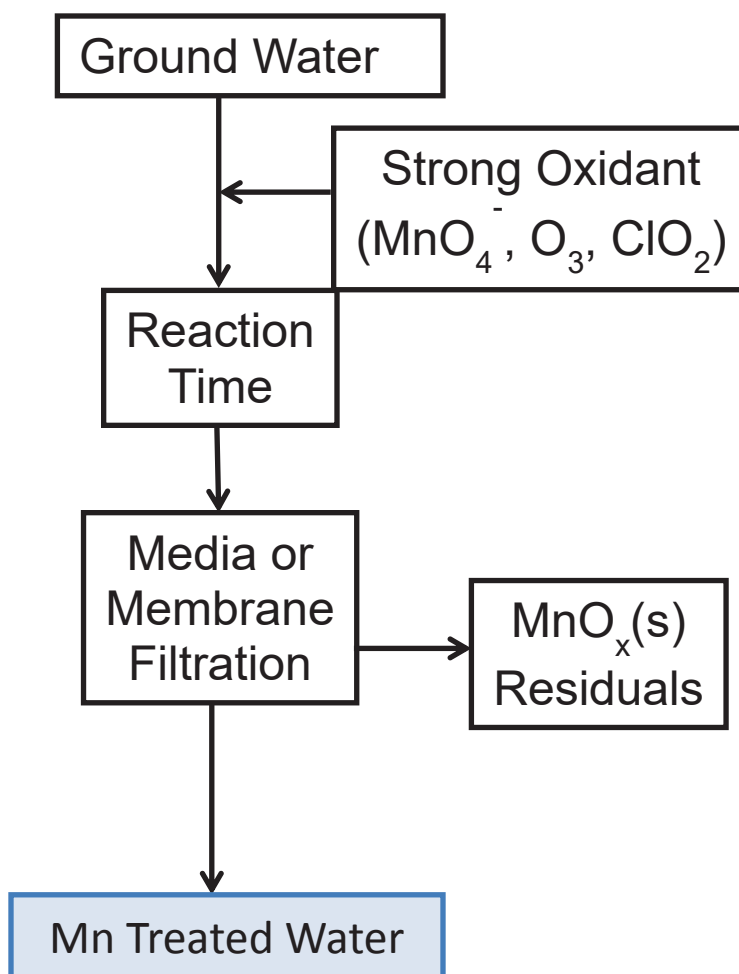


Figure 6.2 Schematic of oxidation and direct filtration of MnO<sub>x</sub>(s) particles for groundwater.

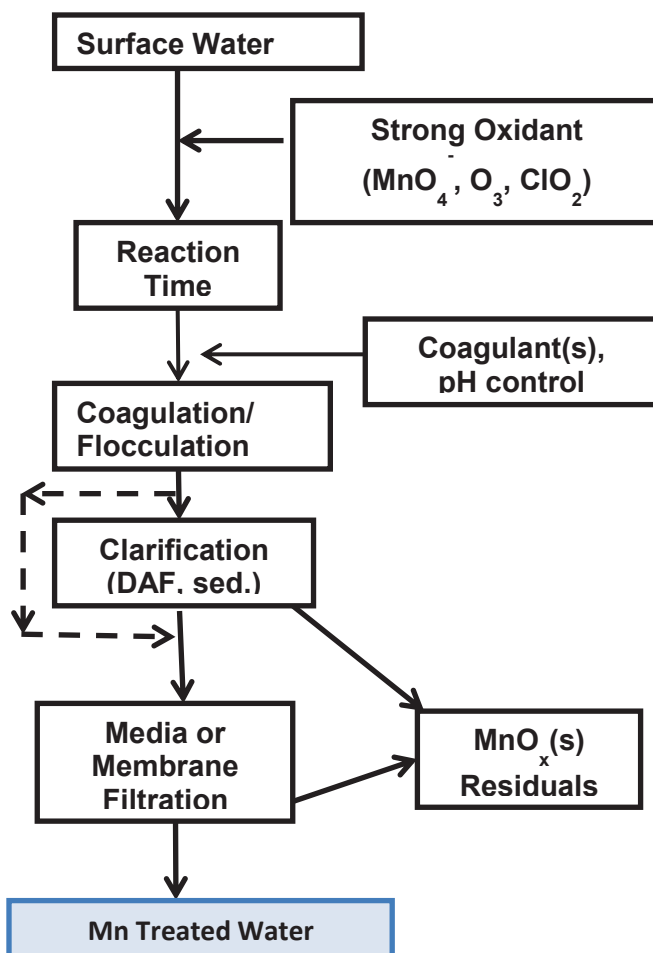


Figure 6.3 Schematic of pre-oxidation treatment for Mn for a surface water.

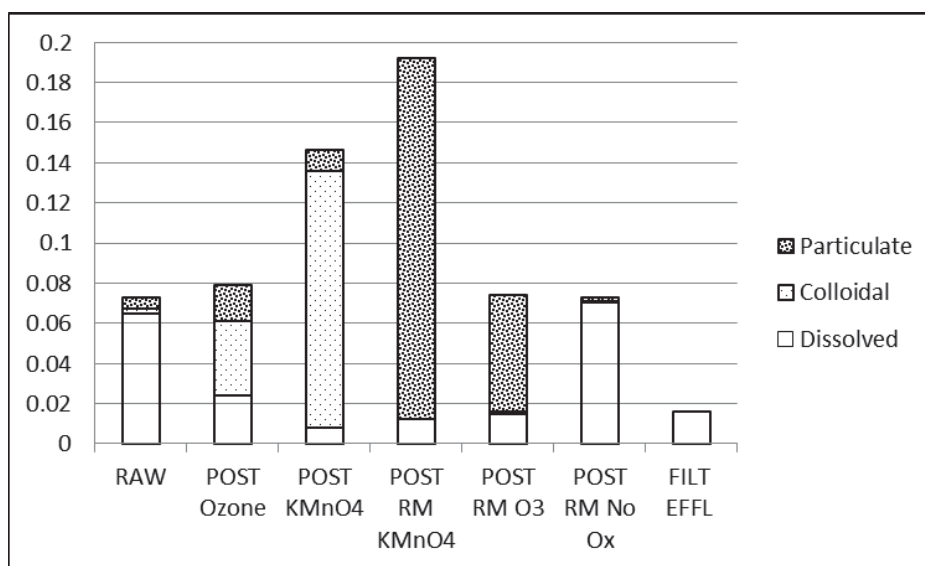


Figure 6.4 Fractionation of Mn; direct filtration with permanganate and ozone pre-oxidation (Tobiason et al 1992)

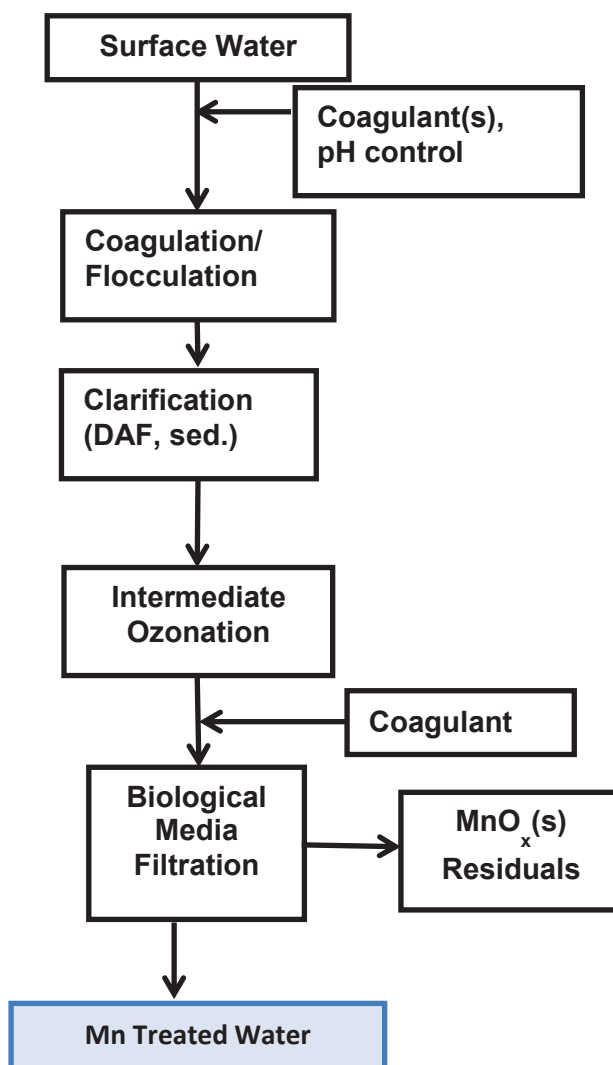


Figure 6.5 Schematic of intermediate-oxidation treatment for Mn for a surface water.

## SORPTION AND CATALYTIC OXIDATION

### Traditional Greensand Process

The traditional means of removing dissolved Mn(II) via adsorptive uptake has been through the use of greensand filtration. Greensand media utilizes glauconite as the base surface followed by chemical deposition of an MnO<sub>x</sub>(s) surface through an oxidation reaction with Mn. The resulting media has a substantial adsorptive capacity for removing dissolved Mn(II) (reported at values approximating 1.5 kg/m<sup>3</sup>). The adsorptive uptake of dissolved Mn(II) occurs with the concurrent release of H<sup>+</sup> ions to solution.

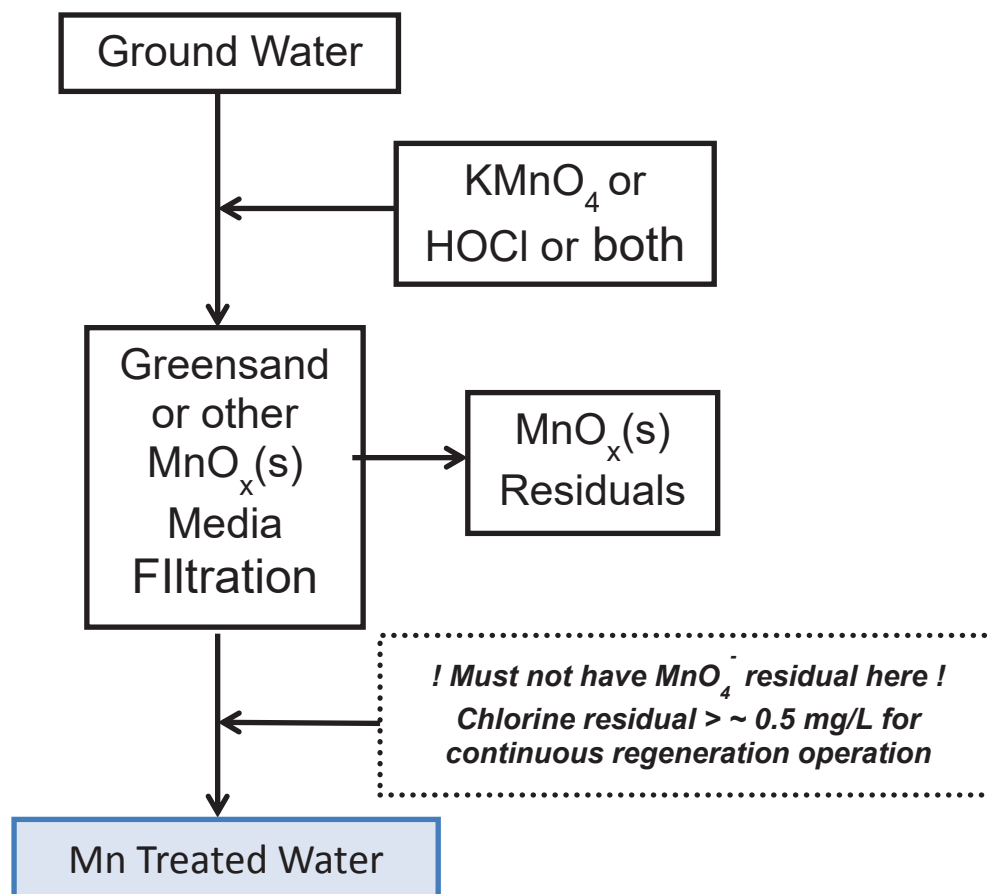


Greensand media has been historically smaller in characteristic size than traditional silica sand, with a sieve analysis of 18 x 60 mesh and an effective size of 0.3 to 0.35 mm (corresponding uniformity coefficient typically below 1.6). The smaller characteristic media size yields very good performance regarding the capture of fine-size particles within the filter bed. However, the head loss generated by the media is likewise significantly higher than an equivalent bed depth of silica sand of larger effective size. As a result, most applications of greensand media have utilized pressure filtration. The greensand media has required chemical treatment after installation to establish the adsorptive capacity of the media surface. This has typically been accomplished by soaking the media in a potassium permanganate ( $\text{KMnO}_4$ ) solution for several hours followed by backwashing to remove residual permanganate from the media.

Greensand filtration systems have traditionally been operated in either a continuous regeneration (CR) or intermittent regeneration (IR) mode for dissolved  $\text{Mn(II)}$  removal. CR denotes the continuous application of an oxidant to the filter-applied water so that regeneration of the greensand media is ongoing at all times; in comparison, IR operation signifies the addition of an oxidant for media regeneration only during offline (non-water-production) times. Historically, most greensand filtration systems have operated in a CR mode, with the traditional oxidant addition being potassium permanganate. The rate of reaction between dissolved  $\text{Mn(II)}$  and permanganate is fast, so much of the dissolved  $\text{Mn(II)}$  is in fact oxidized by the permanganate to  $\text{MnO}_x(\text{s})$  before reaching the greensand media. In these situations the media functions primarily for particulate  $\text{MnO}_x(\text{s})$  removal, with any unoxidized  $\text{Mn(II)}$  being removed by adsorption onto the  $\text{MnO}_x(\text{s})$  surface of the greensand media. Residual permanganate that reaches the greensand surface can promote regeneration of the media. Unfortunately, continuous application of permanganate to the media can ultimately lead to penetration of permanganate through the greensand layer and the production of “pink water”, a condition that must be avoided. [Figure 6.6](#) is a schematic of the greensand type process with continuous regeneration.

A better alternative for greensand media regeneration is to employ free chlorine application to the greensand media in conjunction with lower dosages of permanganate or with no permanganate. Free chlorine can regenerate the  $\text{MnO}_x(\text{s})$  surface on the media by oxidizing the adsorbed  $\text{Mn(II)}$ . Maintenance of at least a 0.5 to 1.0 mg/L free chlorine concentration in the filtered water helps ensure good regeneration of the greensand media. This method of operation is also captured in [Figure 6.6](#).

There are several possible advantages of employing free chlorine for greensand media regeneration. These include lower unit chemical costs, less solids loading to the filter (which results in slower rates of head loss buildup), elimination of the risk of creating “pink water” by excessive permanganate addition as well as possible better overall Mn removal. Of course these benefits must be weighed against the impacts of the formation of regulated DBPs caused by the presence of free chlorine. Additionally, in cases when dissolved  $\text{Mn(II)}$  concentrations are high (>1 mg/L) it may be desirable to maintain the use of permanganate as a preoxidant, forming  $\text{MnO}_x(\text{s})$  particulates which can be removed by the media. Supplementing or replacing permanganate with free chlorine should be phased in slowly, allowing time to assess the consequences on water quality. Ultimately, the potential benefits and impacts of free chlorine regeneration are site specific.



**Figure 6.6 Schematic of Mn removal from groundwater by greensand type processes.**

Typical greensand media depths have been between 18 to 30 inches, with greater depth employed for the IR mode of operation. Often a layer of anthracite coal of significantly larger effective size has been placed on top of the greensand media to aid in retention of particulate matter, also producing improved head loss characteristics during the operational cycle of the greensand filter.

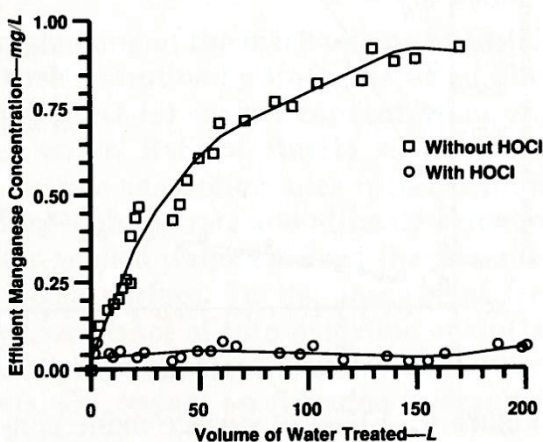
Glaucanite (the basis for greensand media) has historically been mined and processed primarily by one company using a mine located in New Jersey. In recent years mining of glaucanite at this facility has been significantly curtailed for multiple reasons (e.g., evidence of major fossil finds within the mine), such that the traditional greensand media is significantly more difficult to obtain for use in treatment facilities. However, this reduced supply of greensand media has been compensated for by the fact that multiple filtration media manufacturers now produce and sell anthracite coal and silica sand media that has had an  $\text{MnO}_x(\text{s})$  coating applied to the media surface through proprietary chemical processing. These commercially coated media are quite effective at promoting dissolved Mn removal from drinking water; further, the larger size and better structural strength of these media help to minimize some of the negative aspects often seen with the use of traditional greensand media (e.g., more rapid head loss buildup during filter operations). These commercially coated media will likewise increase in  $\text{MnO}_x(\text{s})$  coating level over time by the reactions described in the following section;

as such the dissolved Mn removal capacity of such media will typically increase to a significant degree as the filter media's service life increases.

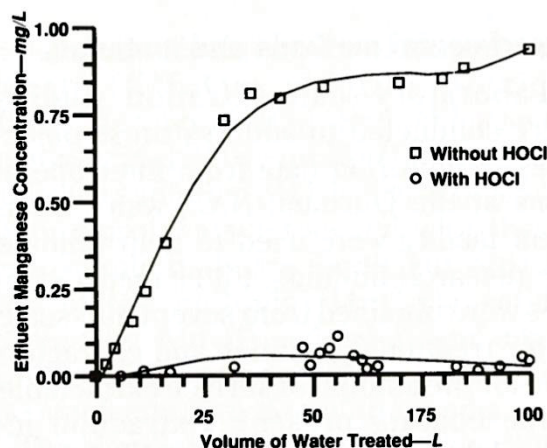
### Mn Removal by MnO<sub>x</sub>(s) Coatings on Conventional Filter Media

Research studies beginning in the late 1980s began to explore the potential for adsorptive uptake of dissolved Mn(II) onto MnO<sub>x</sub>(s) coatings that were found to develop naturally on anthracite coal and silica sand media in water treatment filters. These MnO<sub>x</sub>(s) coatings demonstrated substantial adsorptive uptake capacity for dissolved Mn(II) and were demonstrated to contribute greatly to the overall ability of many water treatment facilities to achieve effective Mn control. Key conditions necessary for this adsorptive uptake process to function on MnO<sub>x</sub>(s)-coated media include:

- Presence of a free chlorine residual in the filter-applied water, with a recommended 0.5 to 1.0 mg/L free chlorine concentration in the filtered water to help ensure effective MnO<sub>x</sub>(s) coating regeneration. The absence of filter-applied HOCl leads to eventual exhaustion of the capacity of the filter media coating for dissolved Mn(II) uptake (representative results in Figure 6.7).
- A filter-applied water pH of 6.0 to 6.2 or higher as lower pH values yield competition for Mn(II) adsorption sites from H<sup>+</sup> ions (enhanced Mn(II) uptake occurs as the pH of the filter-applied water increases).
- Presence of dissolved Mn(II) for adsorptive uptake as the coatings do not necessarily enhance particulate Mn removal.



(a)

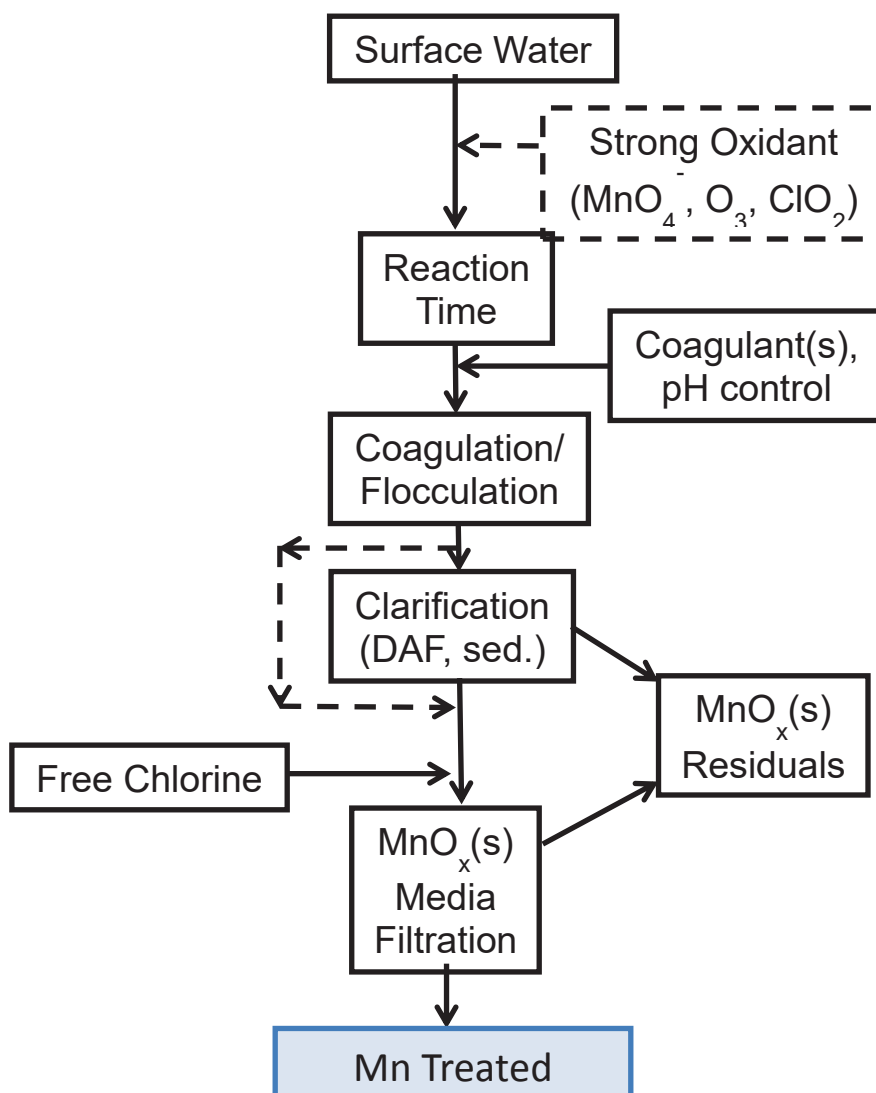


(b)

**Figure 6.7 Removal of dissolved Mn by MnO<sub>x</sub>(s) coated filter media in the presence and absence of 2 mg/L of free chlorine in the applied water at (a) pH (6-6.2) and (b) pH 7.8 (Knocke et al 1991a. Reprinted from *Journal AWWA* by permission. Copyright ©1991 by the American Water Works Association)**

Operation under these conditions routinely results in the highly effective uptake of dissolved Mn(II) onto the MnO<sub>x</sub>(s) coatings, with the filtered water typically having residual

dissolved Mn(II) concentrations at or below 0.015 mg/L (often the concentration may be below the detection limit of the analytical instrument). Such performance levels have been documented across dozens and dozens of full-scale water treatment facilities, in situations having dissolved Mn(II) concentrations as high as 0.5 mg/L in the filter-applied water. In some treatment facilities analytical testing has confirmed that the  $\text{MnO}_x(\text{s})$  coatings on the filter media are the primary means of dissolved Mn(II) removal. In other situations, addition of a strong oxidant to raw or clarified water directly oxidizes a portion of the dissolved Mn(II) to particulate form (as in Figures 6.3 and 6.5), with the  $\text{MnO}_x(\text{s})$  coating on the filter media serving as a secondary, polishing step for achieving very low residual dissolved Mn(II) levels in the filtered water. Figure 6.8 is a schematic of this overall process.



**Figure 6.8 Schematic of surface water treatment with Mn-oxide coated media and pre-filter chlorine addition for dissolved Mn(II) uptake; pre-oxidation may also be used (dashed lines)**



These  $\text{MnO}_x(\text{s})$  coatings develop naturally on anthracite coal and silica sand filter media when the media are exposed to dissolved  $\text{Mn}(\text{II})$  and free chlorine. Unfortunately new, uncoated media may take several days to several weeks to develop sufficient initial  $\text{MnO}_x(\text{s})$  on the media surface to begin yielding effective dissolved  $\text{Mn}(\text{II})$  removal within the filter. As a result commercial media manufacturers now supply filter media that contains an initial amount of  $\text{MnO}_x(\text{s})$  coating, applied by proprietary methods. Water utilities have also developed their own procedures for “soaking” new media in solutions of free chlorine and potassium permanganate overnight to promote initial  $\text{MnO}_x(\text{s})$  deposition on the media surface. Once these initial coatings develop the further uptake of dissolved  $\text{Mn}(\text{II})$ , coupled with free chlorine application results in deposition of additional  $\text{MnO}_x(\text{s})$  on the media surface, enhancing overall dissolved  $\text{Mn}(\text{II})$  uptake capacity of the filter media. While a portion of this coating is dislodged and lost during backwash operations (and greater amounts dislodged through the use of air scour), there is sufficient coating retention to ensure effective dissolved  $\text{Mn}(\text{II})$  uptake once the filter is placed back into service.

Media samples containing an  $\text{MnO}_x(\text{s})$  coating have been chemically extracted and subsequently analyzed by AA or ICP-MS. Extraction typically employs a powerful reducing agent (e.g., hydroxylamine sulfate) under mildly acidic conditions. Typical  $\text{MnO}_x(\text{s})$  coating levels can vary from  $<1$  mg Mn/g media to perhaps 30 to 40 mg Mn/gm media depending upon the historical dissolved  $\text{Mn}(\text{II})$  loading to the filter media and the in-service time of the media. While such coating levels provide substantial dissolved  $\text{Mn}(\text{II})$  adsorptive uptake capacities within the filter, they do not significantly impact the size and density of the filter media. Studies have shown that the presence of such  $\text{MnO}_x(\text{s})$  coatings has no discernible effect on the effective size, uniformity coefficient or the density of either anthracite coal or silica sand based upon the extraction and sieve analysis of media samples from many water treatment facilities. As such the presence of an  $\text{MnO}_x(\text{s})$  coating should not negatively impact the hydraulic behavior of the media, especially during backwashing operations.

The  $\text{MnO}_x(\text{s})$  coatings on filter media also demonstrate a significant affinity for adsorbing other metals, including aluminum, iron, calcium and a variety of heavy metals (e.g., Cu, Zn, Ni, Pb). As such these coatings help to remove certain trace metal species from the treated water. However, the uptake of these metals has not been shown to negatively impact the adsorptive uptake capacity of the  $\text{MnO}_x(\text{s})$ -coated media for dissolved  $\text{Mn}(\text{II})$  removal.

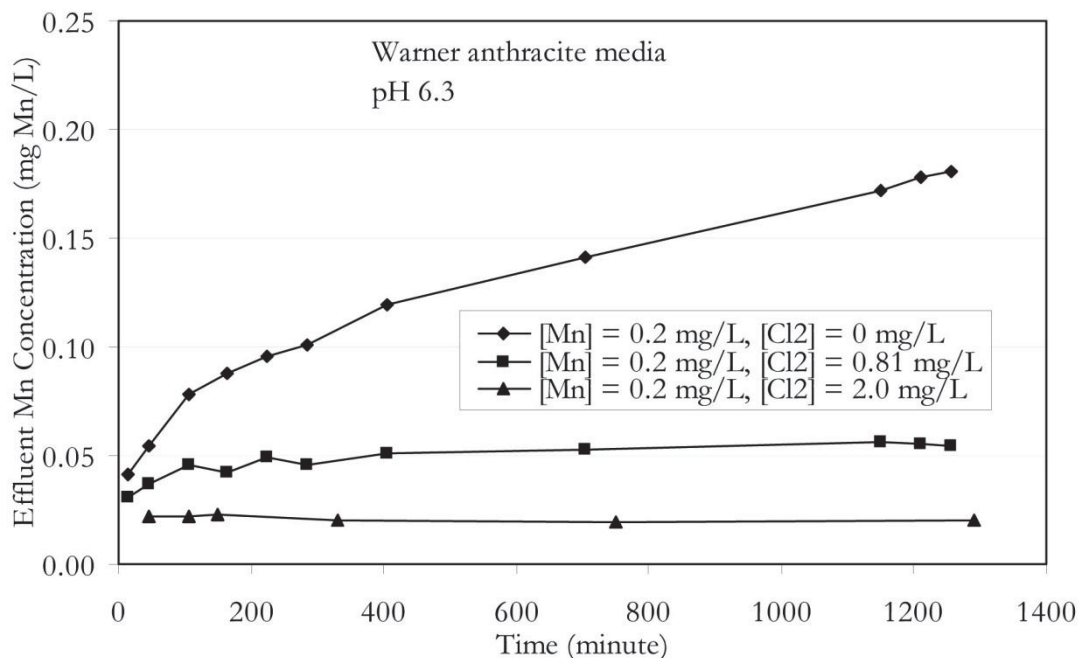
Media with a significant  $\text{MnO}_x(\text{s})$  coating level often demonstrate both high dissolved  $\text{Mn}(\text{II})$  adsorptive uptake capacity as well as kinetically rapid rates of uptake. As a result, most of the dissolved  $\text{Mn}(\text{II})$  present in water is effectively removed within the first six to twelve inches of filter media depth, especially at the hydraulic loading rates typically employed in conventional dual-media filters (e.g., 2 to 5 gpm/ft<sup>2</sup>).

The presence of significant free chlorine (e.g., enough to yield a 0.5 to 1.0 mg/L free chlorine residual in the filtered water) across the  $\text{MnO}_x(\text{s})$ -coated filter media promotes a continuous regeneration of the media surface in a manner similar to that achieved with greensand filtration. If the free chlorine level to a filter is dramatically reduced or even eliminated, the  $\text{MnO}_x(\text{s})$  surface will become saturated with adsorbed, unoxidized  $\text{Mn}(\text{II})$ . The adsorptive uptake capacity of the media becomes exhausted and dissolved  $\text{Mn}(\text{II})$  will begin to appear in the filtered water. While free chlorine may be present in the water applied during filter backwash, the total concentration present as well as the contact times typical of backwash operations would not yield significant regeneration of the  $\text{MnO}_x(\text{s})$  surface. Regeneration of the media would

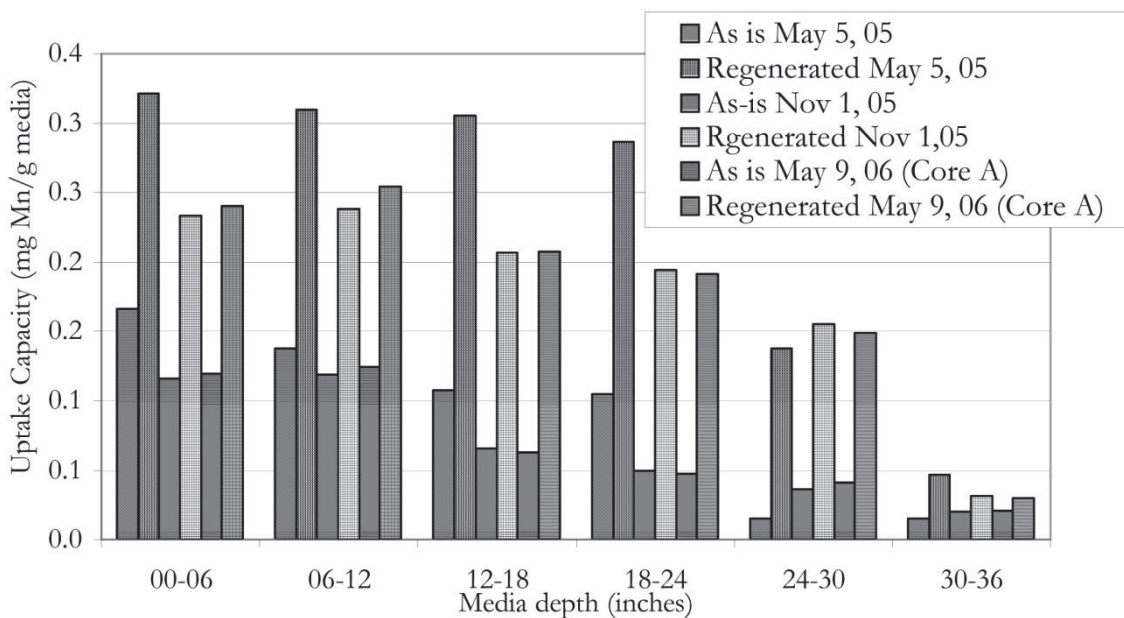
instead need to be accomplished by offline addition of substantial amounts of free chlorine and/or potassium permanganate in order to promote oxidation of the adsorbed Mn(II) present on the MnO<sub>x</sub>(s) surface.

Perhaps the most exhaustive research evaluation of MnO<sub>x</sub>(s) coatings on anthracite coal and silica sand filter media was undertaken by Tobiason et al., (2008). Their work involved the evaluation of MnO<sub>x</sub>(s)-coated filter media from approximately one dozen full-scale water treatment facilities in the United States and the United Kingdom. Cores of filter media samples were collected and analyzed for extractable MnO<sub>x</sub>(s) content as well as dissolved Mn(II) adsorptive uptake amounts, both as removed from the filter as well as after full HOCl regeneration. Key findings of the research effort included the following:

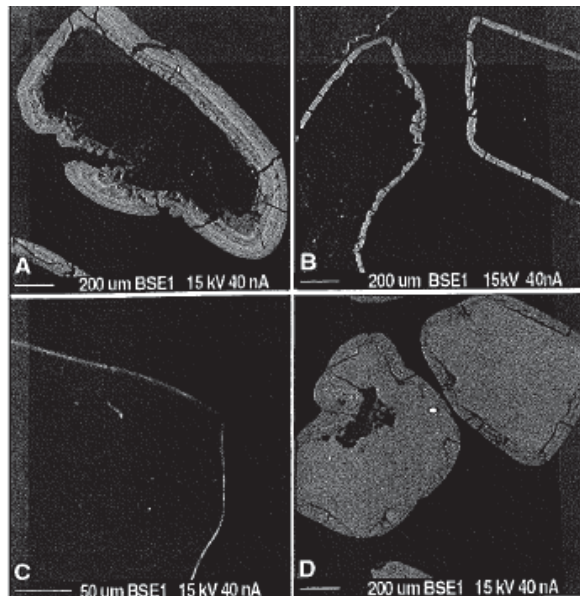
- The presence of significant free chlorine in the filter-applied water was critical to effective dissolved Mn(II) removal across the MnO<sub>x</sub>(s)-coated media (representative results shown in [Figure 6.9](#)).
- The primary removal capacity for dissolved Mn(II) uptake occurs in the upper portion of the filter bed, where likewise the greatest amount of MnO<sub>x</sub>(s) coating is present on the media. This is shown in [Figure 6.10](#) for representative core media samples as a function of media depth. As such the vast majority of Mn(II) removal occurs in the upper reaches of the filter media.
- This dissolved Mn(II) removal capacity remains in place and viable throughout the year. Again, [Figure 6.10](#) demonstrates that very similar levels of Mn(II) uptake capacity were observed within a given bed when sampled at different seasonal times of the year.
- The typical HOCl concentrations maintained across filter media are effective as regenerating a substantial amount of the media's dissolved Mn(II) adsorptive capacity. However, some of that removal capacity is not routinely regenerated by conventional HOCl dosing practices (comparative data shown in [Figure 6.10](#)). Utilities may find that a periodic, offline soaking of the MnO<sub>x</sub>(s)-coated media in concentrated HOCl or potassium permanganate solutions could further enhance the adsorptive uptake capacity of the media for dissolved Mn(II).
- The presence of free chlorine across the filter media can result in a significant increase in DBP formation in the water being treated. The authors presented their own research results as well as the work of other researchers and concluded that the DBP increase could be as little as 10% or over 50% depending upon the specific water being treated. Clearly DBP concerns must be factored into any decision to employ this technique as part of an overall strategy for soluble Mn control.
- Sampling of filters at a variety of water treatment facilities yielded wide variations in extractable MnO<sub>x</sub>(s) surface concentrations on the media. These coating variations are shown in representative scanning electron micrograph (SEM) images of media grain cross-sections shown in [Figure 6.11](#). The coatings are shown as lighter color bands on the surface of the media. Thicknesses range from the order of 50 to 100 μm to just a few μm, with corresponding manganese levels of 30 to less than 1 mg Mn per gram of media. The research also demonstrated that the majority of active soluble Mn(II) adsorptive uptake probably occurred on the outer surface of the MnO<sub>x</sub>(s) coating, as short-term Mn uptake capacity did not consistently increase in proportion to coating levels above a few mg Mn per gram of media. As such, it is not necessary to have substantial amounts of MnO<sub>x</sub>(s) coating present for media to function quite effectively for soluble Mn(II) removal.



**Figure 6.9 Effect of free chlorine on effluent Mn concentration (Tobiason et al 2008)**



Core—filter media samples, Sample source—Harwood's Mill Water Treatment Plant, Newport News, Va  
**Figure 6.10 Temporal variations in Mn uptake capability of media samples as a function of bed depth: Core-filter (Tobiason et al 2008)**



Scanning electron microscopy images of cross sections of anthracite from filter media from (A) the Brown Water Treatment Plant in Durham, N.C.; (B) the William S. Warner plant in Fairfield, Conn.; (C) the Sobrante plant in El Sobrante, Calif.; and sand grains from a first-stage filter in (D) the North Stamford treatment facility in Stamford, Conn.

**Figure 6.11 SEM image of  $\text{MnO}_x(\text{s})$  coated filter media grains (Tobiason et al 2008)**

As mentioned previously  $\text{MnO}_x(\text{s})$  coatings form naturally on filter media due to the presence of dissolved  $\text{Mn}(\text{II})$  and free chlorine across the filter bed. These coatings provide dissolved  $\text{Mn}(\text{II})$  removal while free chlorine is maintained across the filter; however, detrimental effects on water quality can be observed at times when the free chlorine is no longer applied to the filter. Over the past decade, for example, many water utilities have decided for various reasons to implement ozone addition upstream of their filters for disinfection and/or disinfectant byproduct control. Ozone addition will promote the partial oxidation of dissolved organic carbon (DOC) and often increase the bioavailability of that DOC. Water utilities respond to this by implementing biofiltration and encouraging microbial growth on the filter media. In order to achieve such growth the utility will cease adding free chlorine to the filter-applied water. While this allows biofiltration to take hold, many water treatment facilities have also observed an increase in dissolved  $\text{Mn}(\text{II})$  in the filtered water as the  $\text{MnO}_x(\text{s})$  coating becomes a “source” of dissolved  $\text{Mn}(\text{II})$  instead of a method for  $\text{Mn}(\text{II})$  removal. For reasons as yet unknown, the cessation of free chlorine to the  $\text{MnO}_x(\text{s})$  coating can promote significant release of dissolved  $\text{Mn}(\text{II})$  to the treated water. Research has shown that both Mn oxidizing and reducing bacteria can be found in filters with  $\text{MnO}_x(\text{s})$ -coated media, even when significant free chlorine is present in the filter. As such, the conversion to biofiltration appears to stimulate at least a transitional phase of dissolved  $\text{Mn}(\text{II})$  release that can yield unacceptable filtered water  $\text{Mn}(\text{II})$  levels and the potential for consumer complaints due to water discoloration concerns.

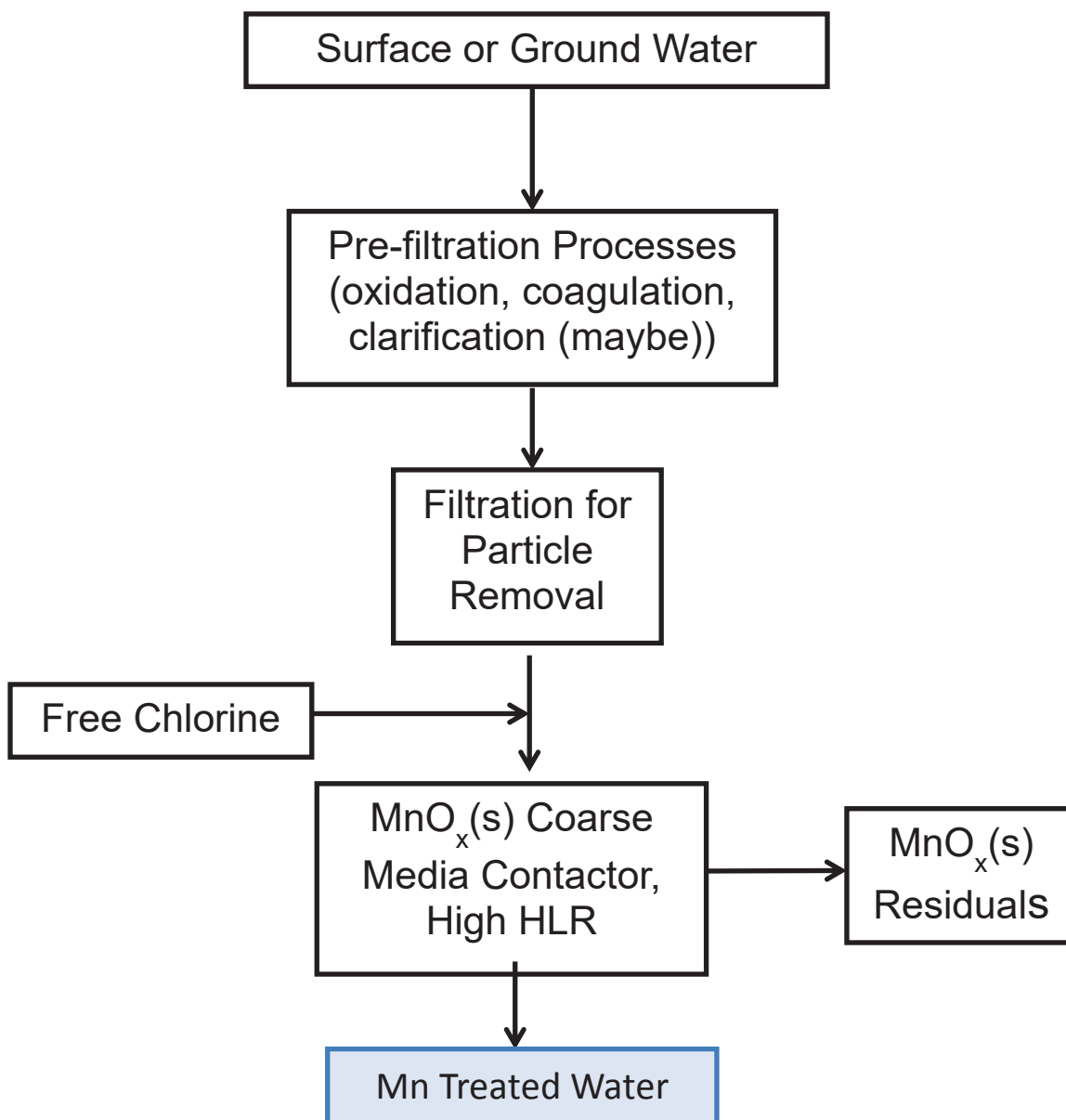


Water utilities that have a known  $\text{MnO}_x(\text{s})$  coating on the filter media will need to approach a potential conversion to biofiltration with substantial caution so as to be alert to the possibility of such a dissolved  $\text{Mn}(\text{II})$  release occurring. Some utilities have responded to this situation by simply replacing all of the filter media to remove the  $\text{MnO}_x(\text{s})$  coating as a source for  $\text{Mn}(\text{II})$  release. Such a media change-out could be quite costly, but may be the only option when converting to biofiltration.

As mentioned previously, one of the key benefits to having  $\text{MnO}_x(\text{s})$ -coated media as part of the treatment train is the ability of this process to generate extremely low finished water dissolved  $\text{Mn}(\text{II})$  concentrations. As shown in the case studies in this manual, water treatment facilities that do not have  $\text{MnO}_x(\text{s})$ -coated media within the treatment train typically are more challenged to consistently produce finished water Mn concentrations of  $\leq 0.015$  mg/L. The introduction of biofiltration at many facilities has eliminated the potential for an  $\text{MnO}_x(\text{s})$  surface to be present on the filter media. Likewise, many water treatment facilities utilize granular activated carbon (GAC) media either as a mono-media filter-adsorber or as a replacement layer for anthracite coal in dual-media filters. Significant  $\text{MnO}_x(\text{s})$  coatings do not form on GAC media due to the inability to have significant penetration of free chlorine into the media. Without free chlorine there is no means of generating the  $\text{MnO}_x(\text{s})$  surface or perpetuating its development through further  $\text{Mn}(\text{II})$  adsorption and surface oxidation.

### **Post-Filter Contactors for Mn Removal**

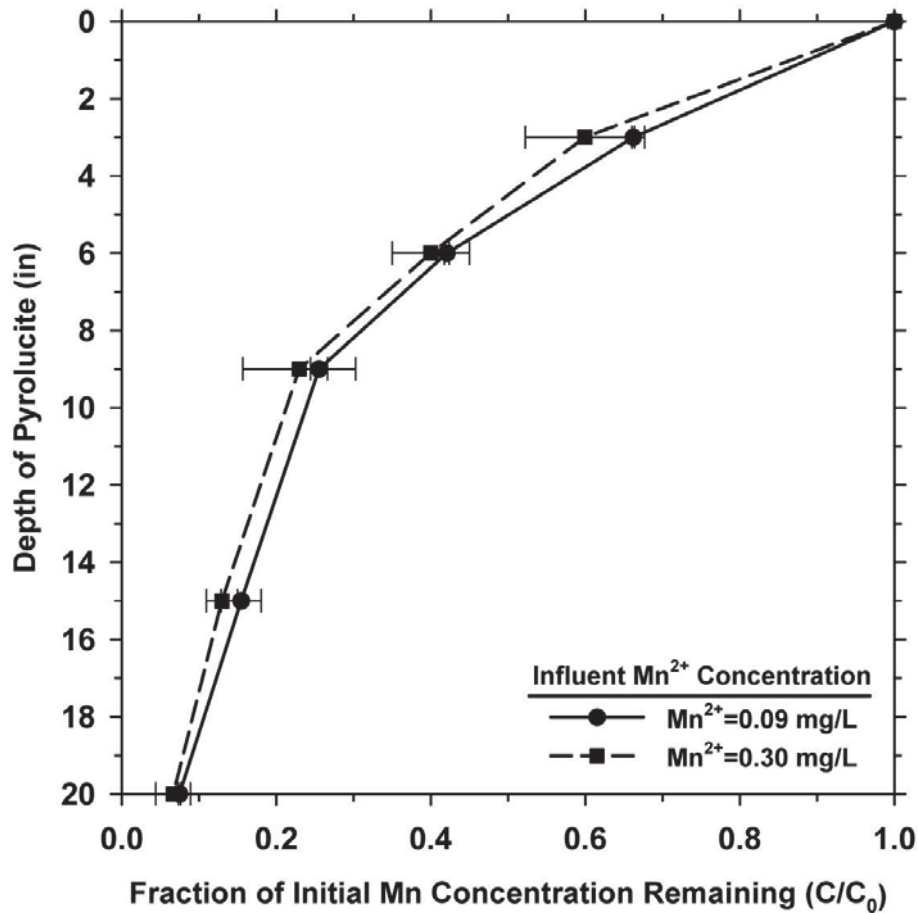
In response to these situations, a new approach has begun to emerge to integrate an  $\text{MnO}_x(\text{s})$ -coated media into the overall treatment train. The concept is that of a post-filtration adsorptive contactor for dissolved  $\text{Mn}(\text{II})$  removal. The contactor would be placed in the overall water treatment train downstream of the filtration step and would employ media of significantly larger effective size (e.g., 1.5 to 3 mm) so as to allow for much larger hydraulic loading rates (10 to 20 gpm/ft<sup>2</sup>) without excessive clean bed head loss. A schematic of this process is shown in [Figure 6.12](#).



**Figure 6.12 Schematic of post-filtration Mn contactor process**

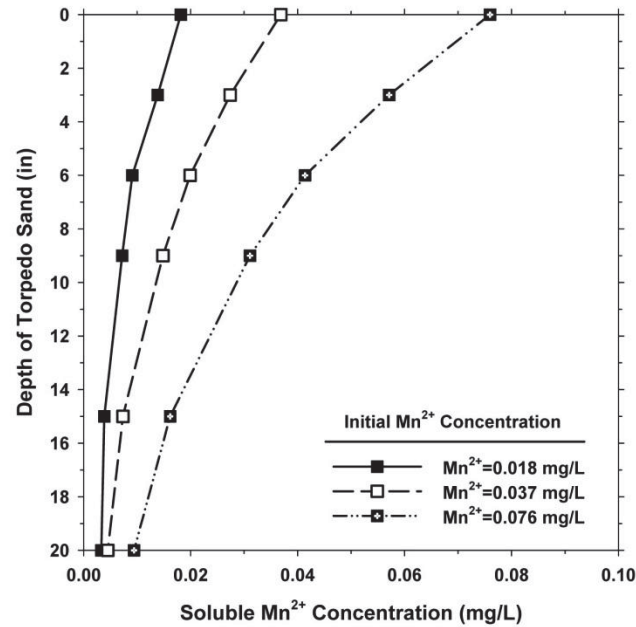
To date, beds of different media types (solid pyrolusite ( $\text{MnO}_2(\text{s})$ ),  $\text{MnO}_x(\text{s})$ -coated torpedo sand,  $\text{MnO}_x(\text{s})$  coated anthracite, a commercial ceramic media with  $\text{MnO}_x(\text{s})$  coating) and depths (up to 40 inches) have been tested on both the bench- and pilot-scale to demonstrate the effectiveness of the post-filtration contactor for removing dissolved  $\text{Mn}(\text{II})$ . A free chlorine residual is maintained across the contactor to promote regeneration of the contactor media surface. Information in Figures 6.13 through 6.16 show representative performance data for bench- and pilot-scale studies, demonstrating the applicability of the approach over a fairly wide range of applied dissolved  $\text{Mn}(\text{II})$  concentrations. As such, the research has demonstrated that the contactor concept can function as both a primary dissolved  $\text{Mn}(\text{II})$  removal method or to supplement upstream  $\text{Mn}(\text{II})$  oxidation treatment by serving as a secondary, polishing step for

Mn(II) control. The high hydraulic loading rates allow for the contactor concept to be implemented without requiring a large amount of overall contactor plan surface area.



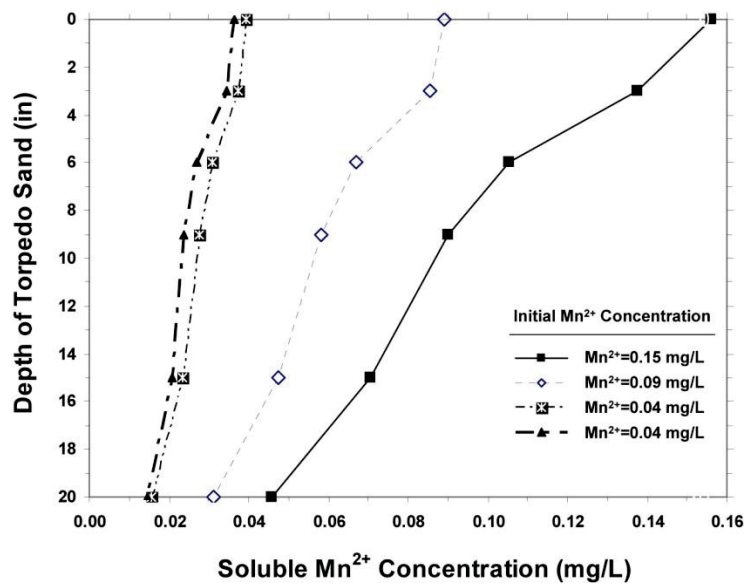
(influent water: HLR=16 gpm/ft², HOCl=1.9 to 2.1 mg/L, pH=7.5 to 7.6)  
C—concentration, HLR—hydraulic loading rate, HOCl—hydrochlorous acid

Figure 6.13 Effect of influent Mn concentration on fractional removal versus bed depth  
(Tobiason et al 2008)



(influent water: HLR=16 gpm/ft<sup>2</sup>, HOCl=1.1 to 1.8 mg/L, pH=7.2 to 7.5)  
BCVPIWA—Blacksburg-Christiansburg-Virginia Polytechnic Institute Water Authority, HLR—hydraulic loading rate, HOCl—hydrochlorous acid

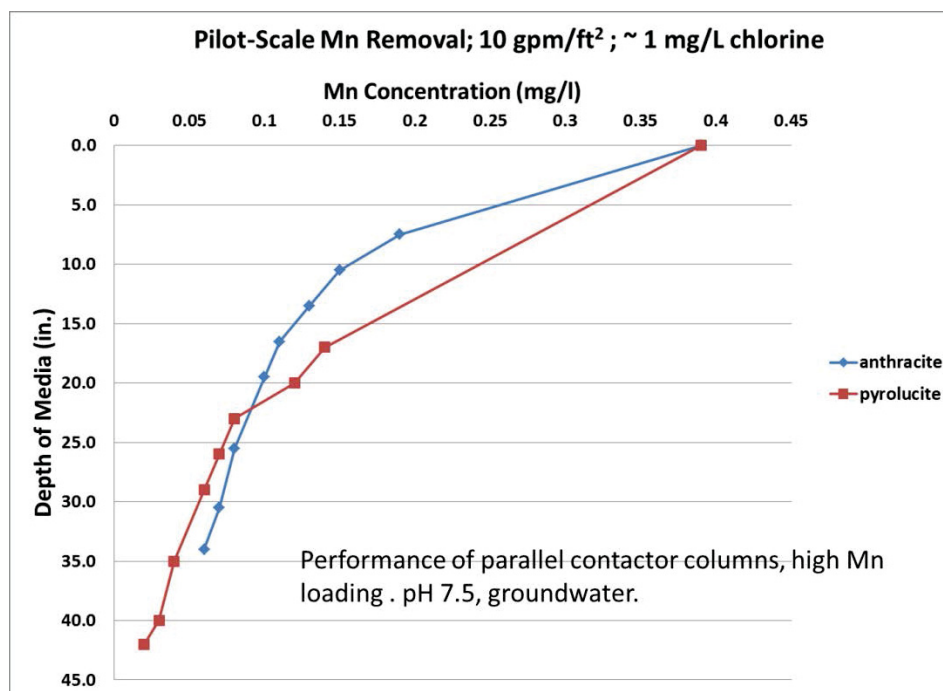
Figure 6.14 Pilot scale dissolved Mn profiles, BCVPIWA (Tobiason et al 2008)



(influent water: HLR=16 gpm/ft<sup>2</sup>, HOCl=1.7 to 3.4 mg/L, pH=7.2 to 7.4)  
HLR—hydraulic loading rate, HOCl—hydrochlorous acid

Figure 6.15 Pilot scale dissolved Mn profiles, Newport News, VA (Tobiason et al 2008)





**Figure 6.16 Pilot-scale dissolved Mn profiles, post-filter contactor, groundwater, Aquarion Water Company**

Design of second-stage contactors for manganese removal involves selection of hydraulic loading rate (HLR), media size and bed depth. The goal is to provide sufficient media surface area for the needed level of uptake of dissolved  $\text{Mn}^{2+}$ . As particle removal is not a goal, larger media can be utilized, resulting in lower head loss, especially for the use of higher HLR which decreases the horizontal area of the contactor. Compared to smaller media, larger media may require a deeper bed depth to achieve the desired removal. If head loss and horizontal area are not a great concern, then smaller media at lower HLR and shallower bed depth may be desired. Performance models are currently being developed to allow for evaluation of trade-offs between these design variables. Also, pilot studies can be utilized to evaluate media types and process variables. The Aquarion Water Company case study in Chapter 7 presents an example of a pilot-study based design of larger sized media contactor for a groundwater source.

While the particulate loading to the contactor is minimal (since the water is filtered upstream of the contactor) pilot-scale studies have demonstrated that the deposition of dissolved  $\text{Mn(II)}$  onto the  $\text{MnO}_x(\text{s})$  surface of the media followed by subsequent oxidation by free chlorine does increase the mass of solids contained within the filter. This results in some level of head loss accumulation over time (typically over several weeks). Consideration must also be given to the expected need for infrequent, yet periodic, backwashing of the contactor to fluidize the bed and remove some of the accumulated  $\text{MnO}_x(\text{s})$  surface coating and restore the head loss encountered to clean bed head loss levels.

The post-filtration adsorptive contactor concept is a unit treatment process that could be designed into a new facility or retrofitted into an existing treatment facility. A retrofit situation would need to carefully consider the hydraulic grade line of the existing treatment facility and could necessitate a need for pumping of the water after mixed-media filtration in order to produce the available head for flowing water through the contactor.

## BIOLOGICAL PROCESSES

In North America the overwhelming majority of water treatment plants accomplish dissolved Mn removal by physical-chemical means of treatment, employing either direct chemical oxidation of the dissolved Mn in solution or adsorptive uptake onto  $\text{MnO}_x(\text{s})$ -coated media. To date only a very small number of water utilities employ biologically based systems for Mn removal; further, these systems are almost all related to the treatment of groundwaters with elevated Mn levels. However, biological methods for Mn removal have been practiced for many years in Europe and report multiple advantages to such an approach. The following text covers the basic principles of biologically based Mn removal systems, addresses some of the reported advantages and challenges of such an approach to Mn control and then presents information on several full-scale water treatment facilities that are employing biological removal methods for Mn.

### Process Principles

Microorganisms that have the ability to promote the oxidation of dissolved  $\text{Mn(II)}$  to insoluble  $\text{Mn(III)}$  and  $\text{Mn(IV)}$  oxide solids exist in numerous environmental settings. Many researchers have stressed the importance of microbes in facilitating the oxidation of  $\text{Mn(II)}$  in natural settings, indicating that among other things, microbial-based  $\text{Mn(II)}$  oxidation can occur as much as 1000 times faster than would occur under abiotic conditions (at near neutral or slightly acidic pH). Many strains of microorganisms have been identified directly or indirectly as having the ability to promote  $\text{Mn(II)}$  oxidation in water, including the proteobacteria *Pseudomonas putida*, a variety of *Leptothrix* species, *Siderocapsa*, *Siderocystis*, the filamentous *Crenothrix* bacterial species, *Metallogenium* and even certain algae, yeasts and filamentous fungi. Some authors argue that the number of microbial species capable of promoting direct or indirect oxidation of  $\text{Mn(II)}$  has been greatly underreported.

Multiple paths for achieving  $\text{Mn(II)}$  removal in biologically-based treatment systems appear possible. Some  $\text{Mn(II)}$  oxidation may be enzymatically driven within or external to the cell structure but removal is not always enzymatically based. Likewise, the accumulation of by-product  $\text{MnO}_x(\text{s})$  resulting from  $\text{Mn(II)}$  oxidation allows for further removal of  $\text{Mn(II)}$  due to adsorptive uptake. As such it is often very difficult to isolate and identify the specific means by which  $\text{Mn(II)}$  removal is occurring in such systems. As an example research studies employing molecular-based methods have shown that certain cultures of *Pseudomonas*, *Leptothrix* and *Bacillus* species utilize a multicopper oxidase enzyme to achieve  $\text{Mn(II)}$  oxidation; further, these species deposit  $\text{MnO}_x(\text{s})$  solids on their cells and/or spores that further  $\text{Mn(II)}$  removal by adsorption.

Mouchet (1992) published an overview of both biologically based Fe and Mn removal processes and practices for drinking water treatment that has been frequently cited. Key points of the paper include:

- Biologically based  $\text{Fe(II)}$  oxidation requires conditions of pH and DO concentration significantly different than that deemed effective for biologically based  $\text{Mn(II)}$

oxidation. Low DO levels are needed under neutral to slightly acidic pH conditions to achieve bioremoval of Fe(II) without allowing direct chemical oxidation to occur. These conditions are much different than the  $\text{pH} > 7.4$  and DO concentration of 5 mg/L or greater cited as being necessary to promote effective biological Mn(II) oxidation.

- As such, Mouchet felt that it would not be possible to achieve biologically based Fe(II) and Mn(II) oxidation within the same biofilter; instead, that two separate biofiltration stages would be required, with pH and DO supplementation occurring between the two stages.
- Several microorganisms are capable of facilitating the oxidation of both Fe(II) and Mn(II) in water.
- In addition to the higher pH and DO levels stated, Mouchet felt that the oxidation-reduction potential (ORP) of the water needed to be at least 300-400 millivolts for Mn(II) oxidation to occur biologically.
- The fact that the removal of Mn(II) is directly by the attached cell mass allows for more rapid filtration loading rates, with hydraulic loading rates at or above 10 gpm/ft<sup>2</sup>.
- Certain substances in water (e.g., elevated ammonia levels, presence of hydrogen sulfide) can be inhibitory to microbial oxidation of Mn(II).

More recent publications have demonstrated that Mn(II) oxidation by biological methods may be more robust than described by Mouchet (1992). For example, one study demonstrated concurrent oxidation and removal of both Fe(II) and Mn(II) in one biofilter (whereas Mouchet indicated that sequential filters would be required to achieve appropriate pH and DO levels for each group of microorganisms). Likewise, research has shown that microbial oxidation of Mn(II) in biofilters treating groundwaters could yield very effective Mn removal with pH conditions as low as 6.4-6.5, well below that recommended by Mouchet. As such the realm over which microbially based Mn(II) oxidation can be achieved may be broader than originally envisioned by Mouchet (1992).

A key issue in establishing a viable microbial population for effective Mn(II) oxidation and removal is the acclimation time required. Growth rates for Mn(II) oxidizing microorganisms are typically much slower than for organisms that promote Fe(II) oxidation. Cited acclimation periods for Mn(II) oxidizers range from as little as 2-3 weeks to requiring upwards of three months to achieve stable, effective Mn(II) oxidation. Water temperature plays a role in the required acclimation period, with longer times being needed when water temperatures are colder (e.g., 9-10 °C). Acclimation times have been reduced through mixing media into new filters from operating filters that were achieving biologically based Mn(II) oxidation. In another study the acclimation period was reduced to a few weeks by inoculating the new filter media with waste biological solids collected from the backwashing of a filter that had active microbial Mn(II) oxidation underway.

Research studies have demonstrated that the presence of ammonia-nitrogen or nitrite can have an inhibitory effect on microbial oxidation of dissolved Mn(II). Biologically based Mn removal was shown to be negatively impacted if either species was present in substantial quantities. Often the Mn(II) removal in the biofilter would first become effective once nitrate began to appear in (and corresponding removal of nitrite from) the effluent water from the filter.

Furthermore, the presence of nitrite has been shown to result in  $\text{MnO}_x(\text{s})$  reduction and subsequent release of  $\text{Mn}(\text{II})$  into solution. Regarding inorganic phosphorus differing results have been noted. In certain waters extremely low levels of phosphate can inhibit microbial oxidation of  $\text{Mn}(\text{II})$  due to phosphorus limitations related to cell growth and synthesis. Research has shown that small additions of phosphorus in waters applied to biofilters can enhance  $\text{Mn}(\text{II})$  oxidation and removal. However, other studies have shown that substantial levels of phosphate can have an inhibitory effect on microbial  $\text{Mn}(\text{II})$  oxidation. Finally, testing has indicated that the presence of reduced sulfide can inhibit microbial  $\text{Mn}(\text{II})$  oxidation.

### **Full-Scale Treatment Examples**

The following are relatively brief summaries of full-scale water treatment systems that are addressing significant issues of  $\text{Mn}(\text{II})$  oxidation and removal from groundwaters using biologically based filtration.

#### ***Woodstock New Brunswick (Canada)***

This facility was one of the very first in North America to treat  $\text{Mn}$ -laden groundwater by biologically based filtration (1999); design capacity was 0.9 MGD. The Mangazur (ONDEO Degremont) process was initially pilot tested prior to full-scale implementation. This process involves the use of a specified filter media coupled with appropriate control of the pH, redox potential and DO concentration in the filter-applied water. The waters to be treated in Woodstock New Brunswick typically had a dissolved  $\text{Mn}(\text{II})$  level of 0.6-0.7 mg/L, a pH of 7.6-7.7 and water temperature of approximately 9-10 °C. Initially the pilot filter hydraulic loading rate was held at 15 m/hr (6.1 gpm/ft<sup>2</sup>) and then increased to 25 m/hr (10 gpm/ft<sup>2</sup>) once effective biological  $\text{Mn}$  removal (quantified as filter effluent  $\text{Mn}$  concentrations below 0.05 mg/L) was achieved. The pilot filter was ultimately operated at 37 m/hr (15 gpm/ft<sup>2</sup>) without loss of effective  $\text{Mn}$  removal. The full-scale facility requires DO introduction prior to the water flowing through the biofilter (design hydraulic loading rate is 25 m/hr (10 gpm/ft<sup>2</sup>)). The full-scale filters required approximately one month for acclimation to occur (yielding filtrate  $\text{Mn}$  levels below 0.05 mg/L). During this acclimation period the full-scale filters were hydraulically loaded at 10-14 m/hr (4-6 gpm/ft<sup>2</sup>). Backwashing of the full-scale filters is done every five to ten days or when maximum acceptable head loss is reached. The biologically based full-scale facility was reported to have cost 60% less than a physical-chemical water treatment plant employing traditional oxidants for dissolved  $\text{Mn}(\text{II})$  oxidation.



### ***Hutchinson, Minnesota***

This facility has a rated design capacity of 6.5 MGD and is focused on softening as well as Fe, Mn and ammonia-nitrogen removal. A portion of the incoming groundwater flow passes through reverse osmosis (RO) treatment and the remaining flow goes through biological treatment, with the effluents from the two treatment approaches being blended prior to release to the distribution system. Raw water Fe values are typically in the 1.5-2.0 mg/L range, raw water ammonia-nitrogen values are typically between 1.4 and 1.7 mg/L and raw water Mn levels are between 0.08 and 0.12 mg/L. The biological treatment train involves two-stage filtration, with pH 7.4 being typical of the first stage of treatment (with lower DO levels) where Fe oxidation is targeted. Raw water going to the first stage has a limited amount of aeration provided to keep DO levels at desired levels. Oxygen is added again along with a minor pH adjustment (closer to 7.7) prior to the water entering the second filtration stage, where the focus is on nitrification and Mn(II) oxidation. A review of operational data from the full-scale facility showed typical effluent values of Fe and ammonia-nitrogen well below 0.1 mg/L and effluent Mn levels typically from 0.015 to 0.03 mg/L. Input from treatment plant personnel indicates a high level of satisfaction with the reliability of the biological treatment train as well as associated costs.

### ***Lake Havasu City, Arizona***

Utility personnel in Lake Havasu City commissioned a pilot-scale evaluation of five alternate Mn removal systems, including greensand filtration, Filtronics electromedia, Mn oxidation coupled with ultrafiltration (UF), ozone addition coupled with standard media filtration and biologically based Mn filtration (using the Mangazur approach). Raw water Mn levels were typically in the 1.1 to 1.2 mg/L range. The biologically based approach was chosen as the most cost effective system for Mn control, with the following observations: process generated less residual solids and these solids were easier to settle and dewater; also, the biological Mn system generated longer filter run times and better overall turbidity removal than the other systems evaluated. The pilot study involved two biologically based Mn filters, one seeded from an existing biological Mn removal plant in France and the other using unseeded media. The seeded media took approximately one month to achieve filter effluent Mn concentrations below 0.05 mg/L, whereas the unseeded filters required approximately six weeks to achieve similar levels of Mn removal. The relatively shorter acclimation periods required may have been associated with the higher Mn concentrations present in the filter-applied water. The full-scale facility was built and completed in 2003 as a biologically based Mn removal system, with design capacity of 26 MGD. The filter hydraulic loading rate as designed was 9 m/hr (between 5 and 6 gpm/ft<sup>2</sup>).

### ***Sorgues, France***

The design capacity of this facility was established at 7.6 MGD. The raw water conditions to be treated included pH of 7.2 to 7.5; dissolved Fe less than 0.1 mg/L, ammonia-nitrogen of 0.2 mg/L and dissolved Mn between 0.7 and 1.0 mg/L. Pilot testing confirmed successful ability to treat the water using the Mangazur approach with filter hydraulic loading rates of 31 m/hr (12.7 gpm/ft<sup>2</sup>). The treatment train involved pressurized in-line aeration (for DO concentration attainment), four biologically based filters and use of chlorine for water disinfection after filtration. A portion of the filtered water was not chlorinated and, instead,

stored for use as backwash water to minimize the potential impacts on the microbes from using chlorinated backwash water. Residual solids collected from the backwash waters were thickened, conditioned with a polymer flocculant and then dewatered by centrifugation. Filters in the full-scale plant that were seeded from waste wash waters from an operating biological Mn removal plant became acclimated and yielded effective Mn removal in approximately one month. In comparison, filters that were unseeded required approximately two months of acclimation prior to achieving effective Mn removal. Once acclimated the typical water quality was less than 0.02 mg/L Mn present in the filtered water. Also, an experimental study demonstrated that even after a two-month shutdown the Mn removal capacity of a filter could be completely restored in approximately five days after restart of the filter.

Treatment of groundwaters containing elevated dissolved Mn concentrations has been undertaken at multiple locations in Japan using the proprietary CHEMILES treatment approach developed by the NAGAOKA Corporation. The process requires the injection of air in specialized nozzles to the filter-applied water, resulting in near-saturation DO concentrations. This promotes rather rapid oxidation of any dissolved Fe(II) in the water, referred to as “contact oxidation” onto the upper stages of the sand filter media. Microbial testing has identified multiple microorganisms (including several *Leptothrix* species as well as *Gallionella*) being present on the filter media, organisms that have been identified as having the ability to oxidize both dissolved Fe(II) and Mn(II). Mn removal (and ammonia-nitrogen removal as well) are then achieved via biological oxidation means. Filter hydraulic loading rates for design purposes are cited as between 5 and 16.7 m/hr (approximately 2 to 7 gpm/ft<sup>2</sup>). Limited data available on acclimation period showed this required under two months to achieve effluent Mn values below 0.05 mg/L. Raw waters containing Fe levels as high as 19.2 mg/L and Mn levels up to 3.3 mg/L were able to be treated and produced filter effluent water qualities of residual Fe less than 0.1 mg/L and Mn below 0.05 mg/L (often at or below 0.02 mg/L).

To date the vast majority of biologically based Mn removal systems reported on in the literature have focused on groundwater treatment situations. These are probably the best cases for justifying microbial-based Mn removal as an alternative to the more traditional physical-chemical approaches that are employed. Groundwaters typically have relatively stable water quality with respect to parameters such as Mn content, temperature and pH. As such, the relative concentrations of dissolved Mn applied to the biofilter are not changing substantially from day to day or week to week. In comparison, facilities treating surface waters may find that influent dissolved Mn concentrations vary greatly over time, with elevated concentrations seen perhaps in the summer and fall months and much lower dissolved Mn levels occurring in the winter. Likewise, the temperature range during the year may be very wide and could lead to organism stress during the cold winter months. The viability of the Mn(II)-oxidizing microorganisms during extremes of dissolved Mn loading as well as temperature variations is uncertain. Also, how long it may take a viable population of Mn(II)-oxidizing microorganisms to acclimate within the broader biofilter community (especially under conditions of variable dissolved Mn(II) loading) is not addressed effectively in the published literature.

As a result, it is difficult to find examples of full-scale facilities treating surface water sources with effective microbial oxidation of dissolved Mn(II). A recent Water Research Foundation report (Kohl et al 2012) included information on a few surface water facilities wherein biologically based Mn(II) oxidation was believed to be occurring. One of those facilities was the Manchester (New Hampshire) water treatment plant. This facility had

ozonation included in the treatment train just upstream of either granular activated carbon (GAC) filters or anthracite-capped filter media. Testing for dissolved Mn concentrations upstream and downstream of the GAC filters showed perhaps an average of 30 to 40% removal; however, the removal was at times very inconsistent and even showed a slight increase in dissolved Mn when comparing the treated to filter-applied water. Also, it is worth noting that the data reported represented only situations where the dissolved Mn levels in the water applied to the GAC media was always below 0.05 mg/L (and at times was below 0.02 mg/L). No data were reported for conditions of dissolved Mn loading at or above 0.05 mg/L. Thus, the performance of the GAC-based biofilter for more elevated dissolved Mn levels could not be evaluated. Finally, the parallel studies using anthracite-based filter media for biofiltration did not show consistent evidence of dissolved Mn removal. The report also included data from the Pennichuck Waterworks Treatment Plant where GAC filter media were employed. At this facility the filter-applied water was often at or below pH 6.0. Results reported for the facility showed minimal (< 5%) dissolved Mn removal occurring across the media.

## SEQUESTRATION

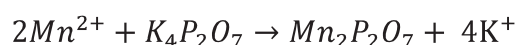
Chemical sequestration is the formation of solution phase complex or chelate between a metal cation and a multi- or poly-dentate ligand (anionic); the latter is known as the chelating or sequestering agent. The goal of sequestration is to prevent the interaction of the metal ion with oxidants or other ligands in order to prevent oxidation and/or precipitation. The chelating agent can form more than one bond or interaction with the metal ion, resulting in a stronger complex than that formed with a simple monodentate ligand (anion).

As the negative aesthetic impacts of Mn in finished drinking water are associated with undesired/unplanned oxidation of reduced Mn(II), sequestration of the  $Mn^{2+}$  cation has the potential to prevent these negative impacts without removal of the Mn. The same rationale applies to sequestration of reduced iron, Fe(II), or  $Fe^{2+}$ .

### Sequestering Agents and Dosing

Common sequestering agents used in drinking water treatment include various polyphosphates which are chains, rings or branches of connected phosphate molecules. The simplest polyphosphate is diphosphate, commonly referred to as pyrophosphate, or diphosphoric acid,  $H_4P_2O_7$ . The next larger polyphosphate is tripolyphosphate or triphosphoric acid,  $H_5P_3O_{10}$ .

The stoichiometry of the reaction of sequestering agents with cations is important for estimating sequestration dosing. As with oxidant dosing, the dose depends on the concentration of  $Mn^{2+}$  as well as the concentration of other cations, especially  $Fe^{2+}$ . The reaction stoichiometry can be illustrated by considering the reaction between the tetrapotassium pyrophosphate salt and reduced Mn as shown below:



The reaction shows that one mole of phosphorus, usually expressed as phosphate by manufacturers, complexes with one mole of Mn. Considering atomic and molecular weights, one basis for polyphosphate dosing is that the stoichiometric dose is approximately 2 mg of

sequestering agent as phosphate ( $\text{PO}_4^{-3}$ ) per mg of Mn(II). The same ratio holds for Fe(II) due to similarity in atomic weight, so baseline stoichiometric dosing is 2 mg as phosphate per mg of combined Mn(II) plus Fe(II). The common major divalent cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  do not form as strong complexes as the reduced Fe and Mn but do impact sequestration dosing as hardness increases. Monovalent cations ( $\text{Na}^+$  or  $\text{K}^+$ ) are not complexed by the polyphosphate species.

Studies have shown that the complexation reaction is very fast, with no added benefit of increasing reaction time prior to oxidant addition beyond 30 seconds. It is important, however, that the sequestering agent be dosed prior to dosing of a disinfectant (Robinson et al. 1990). Sodium silicates are also used as sequestering agents. These products de-polymerize fairly rapidly after addition to water yet have been found to be effective for iron sequestration if chlorine is added very soon after the silicate (Robinson et al. 1987). However, silicates were generally not found to be effective for Mn sequestration (Robinson and Ronk 1987; Robinson et al. 1990). As is the case for addition of phosphate based corrosion inhibitors, addition of polyphosphate sequestration chemicals may increase the potential for increased biological activity with the distribution system.

### Assessing Sequestration Effectiveness

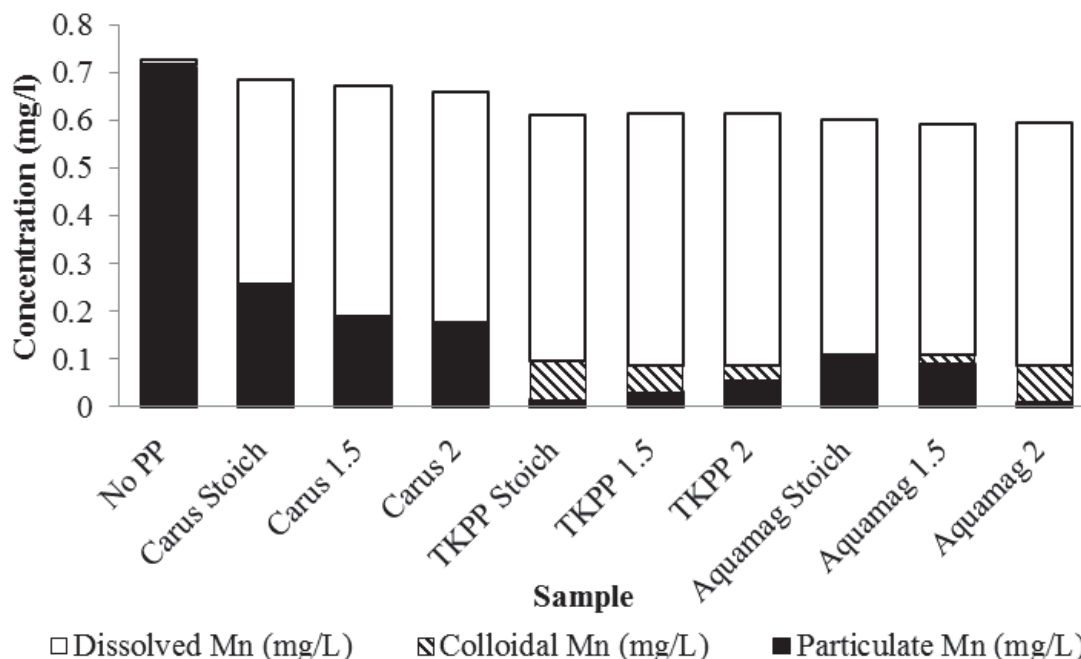
Despite the use of sequestering agents to form chelates with reduced Mn(II), it is currently not possible to directly distinguish between uncomplexed  $\text{Mn}^{2+}$  and chelated Mn in samples of water dosed with sequestering agents. Relatively weak complexes are formed which are easily disrupted by laboratory analytical separation and assessment methods. As a result, an operational approach is used to assess sequestration effectiveness. Samples of raw water are dosed with sequestering agent prior to dosing for pH control and disinfection (e.g., free chlorine). After selected reaction times, samples are assessed for total and combined colloidal/dissolved Mn by filtration through a 0.45 micron membrane filter; fractionation between colloidal and dissolved Mn using ultrafiltration membranes is also desirable. The extent of sequestration effectiveness is based on the fraction of total Mn (or iron) that remains in the colloidal/dissolved fraction after the selected reaction period. Reaction periods of one to several days are appropriate based on typical water age in distribution systems.

Assessment of sequestration effectiveness within a system can be made by fractionation of Mn in system samples as well as comparison of distribution system levels with raw water levels. Two conditions can indicate that sequestration has not been effective at maintaining Mn in the colloidal/soluble form. One condition is when the manganese in samples is mostly in particulate form; if in addition the sample total Mn level is greater than the raw water level, then the process of sampling has likely resulted in scouring of Mn solids that had deposited in the distribution system. The other condition that shows sequestration failure is when total Mn levels are much lower than raw water levels and the remaining Mn is mostly colloidal/dissolved; this strongly suggests loss of particulate Mn in the distribution system. As noted elsewhere, recent studies show that in the presence of oxidant, such as chlorine, and for significant treated water Mn levels, the concentration of Mn typically decreases within the distribution system, showing the system to be a repository for oxidized Mn. While flushing programs can remove such deposits, a better control is to remove Mn during treatment instead of attempting to sequester against eventual oxidation and precipitation. The same rationale also applies to iron sequestration.



Studies have shown that sequestered metals may actually be in oxidized form but remain as very small colloids, stabilized by surface complexation of the negatively charged sequestering agents. It appears that this is typical for iron sequestration (as Fe(II) is so readily oxidized) and can occur for Mn as well (see Robinson et al. 1990 AwwaRF report as well as Lytle and Snoeyink 2002).

Representative results from recent research at University of Massachusetts supported by Aquarion Water Company (Volpe 2012) are shown in [Figure 6.17](#). This example is for a groundwater with 0.68 mg/L of Mn(II) and 0.38 mg/L of Fe(II); the pH was 8. Free chlorine was dosed at 2.5 mg/L and samples were assessed after a 48 hour reaction period. Chemical dosing was undertaken in the field using careful techniques to avoid inadvertent contact with atmospheric oxygen. The results show that without polyphosphate addition, 100% of the Mn was oxidized to particulate form while the three sequestering agents at various doses succeeded in sequestering an average of 83% of the raw water Mn, almost all in the soluble form. Data for iron (not shown) reveal very poor sequestration in general and only sequestration in colloidal form in some cases. In practice, the utility uses oxidant addition and filtration to remove Mn and iron, not sequestration.



**Figure 6.17 Assessing effectiveness of Mn sequestration on groundwater source. Sequestering agent dose = 1x, 1.5x and 2x stoichiometric (Volpe 2012)**

## INTEGRATION OF MANGANESE CONTROL WITH OVERALL TREATMENT

Control of the level of Mn in finished drinking water is rarely the only objective of a water treatment facility. Thus consideration of processes for Mn removal must be integrated with overall treatment goals, usually involving several or many specific treatment objectives. There can be trade-offs between process selection and process economics in order to meet all treatment objectives. This section of Chapter 6 describes some of these issues related to control of Mn.

Fundamentally, Mn control is integrated within a treatment facility because the process options for treatment of Mn are also options for, or have impacts on, options for other treatment objectives. Mn treatment may involve one or more of the following general process options or issues:

- Addition of a chemical oxidant that may also be a disinfectant.
- Need for reaction time and possibly pH control.
- Parallel reactions of oxidants with Mn(II) and multiple other reactants.
- Removal of particulate matter via clarification and/or filtration.
- Need for destabilized particles for media filtration.
- Use of a packed bed of granular media that utilizes energy (head or pressure loss) and must be backwashed in some manner.

- Removal of Mn in particulate form creates a potential source for Mn during residuals processing.
- Need to provide appropriate general water quality conditions for effective biological treatment.

In general, integration of Mn control within overall treatment depends very much on specific aspects of a source water and the context of the treatment facility (e.g., flow capacity, sole facility or part of a multi-facility system, etc.). However, a few common issues are addressed here.

## **Oxidant Dosing**

For Mn control via chemical oxidation and particle removal, dosing of the chemical oxidant is the key process control parameter. Required dosing for oxidation is controlled by the concentrations of all the species that the oxidant will react with, including the targeted Mn(II). Temporal variations in water quality can make it challenging to apply the optimal required dose. In addition, each oxidant has related impacts/constraints on the maximum dose that can be applied. Thus, under and over dosing of oxidants is possible. Overdosing of permanganate results in pink water and undesired/uncontrolled later formation of  $\text{MnO}_x(\text{s})$  particles. Overdosing of ozone can also cause pink water ( $\text{MnO}_4^-$  formation) and may be driven by the need for a specific ozone residual to meet disinfection goals; designers and operators should be cognizant of this potential conflict. Chlorine dioxide dosing may be limited by the formation of the regulated chlorite DBP; the potential for Mn(II) oxidation dosing demand to exceed allowable chlorine dioxide dosing must be considered (multiple oxidant dosing may be required).

## **Chlorine and DBPs**

Perhaps the most robust and operationally convenient method for achieving low finished water Mn concentrations is the use of a Mn oxide granular media surface in the continuous presence of a significant (perhaps  $> 0.5 \text{ mg/L}$ ) free chlorine residual. As described earlier in this chapter, this can occur for traditional greensand filters, for anthracite and sand media in conventional filters for particle removal and in dedicated post-filter, coarse media, high-rate contactors.

Unfortunately, free chlorine also reacts with natural organic matter to form DBPs, some of which have prescribed maximum contaminant levels (e.g., total trihalomethanes (TTHMs) and five of the haloacetic acids (HAA5)). Thus an important consideration for implementation of the sorption/catalytic oxidation method for Mn removal is that NOM levels should be minimized prior to use of this approach. For many groundwaters, NOM levels are low so there is no significant potential for DBP formation. For surface waters, interaction of chlorine with NOM has traditionally been minimized by removal of TOC during coagulation/flocculation/clarification prior to media filtration with pre-filter chlorination and Mn oxide media surfaces.

As described earlier in this chapter, another emerging option for further minimizing chlorine/NOM impacts is to separate the sorption/catalytic oxidation process from the particle

filtration process by using a dedicated post-filter media contactor. This option allows for use of this very robust Mn removal process in cases where upstream media filters are engineered for biofiltration to achieve various objectives, including decreasing TOC levels, which may further minimize the potential for halogenated DBP formation. Dedicated contactors for Mn removal in conjunction with free chlorine disinfection might also be applicable following alternative or advanced treatment technologies that are effective for TOC removal but not for removal of Mn(II); examples include anion exchange and granular activated carbon.

### **Control of Manganese in Residuals**

Ultimately, most Mn “leaves” treatment facilities in the form of particulate Mn oxides. Unfortunately, during residuals processing it is possible to provide opportunities for conditions to occur that facilitate the release of reduced Mn(II) back into the solution phase, possibly exacerbating the challenge of Mn control. One common occurrence of this in the main treatment train is from settled sludges in sedimentation basins; decreasing the residence time of settled sludges must be implemented to control this phenomenon. Sludge may be thickened and/or dewatered, creating a liquid sidestream (lagoon overflow, thickener supernatant, filter pressate, centrate from a centrifuge, etc.) that may contain elevated levels of dissolved Mn(II). Recycling of these streams may introduce dissolved Mn to the head of a treatment plant; if the plant is utilizing pre-oxidation for Mn(II) oxidation it is important that the recycle stream be returned upstream of the oxidant addition. In general, recycle of particulate Mn is not a problem as those particles will be removed by solid-liquid separation processes; however, the recycled solids will add to the total Mn loading of settled residuals, presenting an increased potential for Mn(II) release if not properly managed.

### **Release of Mn from Media Surfaces**

The ability of  $\text{MnO}_x(\text{s})$  surfaces to adsorb Mn(II) and catalyze its oxidation is often used in the removal of Mn from drinking water. In general, the presence of a free chlorine residual and solution phase Mn(II) in water flowing through granular media, tanks or piping will eventually result in the accumulation of an Mn-oxide surface coating, whether that is planned for (engineered) or not. For example, Mn-oxide surfaces can accumulate in the absence of source water Mn when ferric coagulant is used and there is pre-filter chlorination. Unfortunately, the presence of the Mn-oxide surface also provides the potential for the release of Mn(II) through reductive dissolution of the surface (recall that Mn(IV) is insoluble and Mn(III) solids have very limited solubility). In the absence of sufficient free chlorine, reducing conditions may develop (most likely from biological activity; Mn(IV) is an available electron acceptor if oxygen and nitrate are not available) and Mn(II) release may occur.

Utilities must consider potential Mn(II) release when process changes are made that result in the permanent or intermittent elimination of free chlorine in contact with previously created Mn-oxide surfaces. Mitigation steps may involve removal of the Mn-oxide surface coating from a bed of granular media, complete replacement of filter media, continuous provision of a minimal level of chlorine that prevents release from occurring, intermittent use of higher levels of free chlorine, or otherwise providing an environment that either prevents reduction of Mn(IV) or is able to re-oxidize released Mn(II) before it enters the main process



flow. The return to use of free chlorine may be directly in opposition to process changes that were made to decrease formation of chlorinated DBPs and/or promote biological activity in media filters; cases of the impacts of WTP upgrades to intermediate ozonation and bioactive filtration are noted elsewhere in this manual (see Chapter 7 case studies for Newport News, VA and Metropolitan Water District (MWD) of Southern California). As industry knowledge increases, careful control of conditions to promote biological Mn oxidation may be able to both remove Mn(II) from solution and prevent its release from Mn-oxide surfaces.

## OTHER RECOMMENDED RESOURCES

Sommerfeld E.O. *Iron and Manganese Removal Handbook*. American Water Works Association, 1999.

Chapter 14 in, HDR Engineering, *Handbook of Public Water Systems*. John Wiley & Sons, 2001.

Mouchet, P., 1992. "From conventional to biological removal of iron and manganese in France", *Journal American Water Works Association* 84 (4), 158-167.

## CHAPTER 7 CASE STUDIES

The purpose of this chapter is to present a series of utility case studies that illustrate several of the Mn control options described in this manual.

### CITY OF WESTMINSTER, CO

**Problem:** Lake source water contains highly variable Mn with hourly and seasonal spikes, making control of finished water Mn difficult.

**Solution:** Plant utilizes ORP measurements for closed-loop control of permanganate feed used to oxidize Mn.

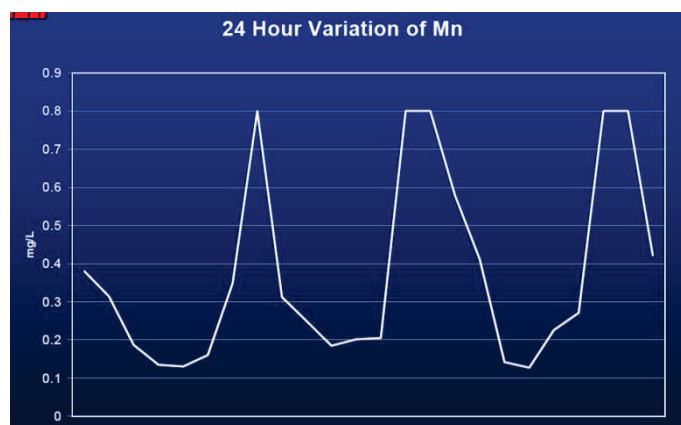
#### *Background*

The City of Westminster raw water supply is relatively pristine high mountain water that is diverted from Clear Creek and transported by canals to be stored in Standley Lake. A 43,000 acre-foot reservoir, Standley Lake is a City park and recreational facility so the City has an interest in protecting the natural ecosystem in the lake. Standley Lake is approximately 87 ft deep at the dam and the intakes to the water plants are located at depths of 82 ft and 57 ft, but the utility only uses the lower intake. Westminster has elected to use the lower intake because it has found the Mn levels in the hypolimnetic layer of the lake treatable (with fairly tight control). If Westminster were to use the upper intake, the potential for bringing algae and increased taste and odor compounds into the plants would be significantly increased and the associated treatment issues would be more complex (not as treatable). By continually pulling water from the lower portion of the lake, the City is reducing the internal recycle of nutrients and the associated loading at turnover to the algae blooms near the surface, thereby helping to preserve the ecology of the lake.

Seasonally, Standley Lake thermally stratifies and hypolimnetic anoxia develops, reducing the DO to  $\leq 2$  mg/L. The raw water pH decreases from around 8 to 7.0 or less during stratification along with increases in iron and Mn dissolution. Dissolved Mn levels during the anoxic season range from 0.5 to 1.5 mg/L.

Westminster currently operates two water treatment plants. One is a conventional ferric coagulation plant and the other is a relatively new pressure micro-filtration membrane plant. Historically, the utility controlled Mn with flow-paced chemical addition under the assumption that raw water Mn was fairly stable in a 24-hour period. Dosage adjustments were made daily based on finished water  $\text{Mn}^{2+}$  levels. Using this method, the finished water Mn varied in a wide range below the 0.05 mg/L secondary standard, with the utility goal set to maintain Mn at 0.02 – 0.03 mg/L. When Mn was tracked in the raw water drawn from the lower intake, Westminster found that the variation of Mn concentration over a 24-hour period was significant, as can be seen in [Figure 7.1](#). In fact, Mn in Standley Lake can fluctuate from 0.02 mg/L to 1.0 mg/L within an hour.

Pilot testing for the new membrane plant forced a hard look by the utility at controlling Mn because the membranes cannot remove dissolved organics, nor is it wise to have oxidation of metals on the surface of the membranes. The pretreatment process for the membranes had to be consistent in oxidizing Mn.



**Figure 7.1 24 Hour variation of Mn in Standley Lake water**

### ***Developing the ORP Installation and Control Approach***

Westminster has no other reasons to consider alternatives to using permanganate for dissolved Mn oxidation. The water is generally low in TOC (<2 mg/L), TTHM < 30 µg/L, HAA5 < 20 µg/L and has no color, so there was no impetus to consider stronger oxidants for other treatment goals. In their approach to testing ORP as a method of control for permanganate, they knew that the  $\text{MnO}_4^-$  oxidation reactions should be measurable with ORP as long as the downstream sampling point was correctly located at a point where no other oxidants were present. The idea was to use the ORP reading as a set point in an electronic loop control to determine the permanganate dose. The utility tested ORP control in the membrane pilot process, then tested it again at full-scale in the conventional plant before final adoption for use in both plants.

To develop target ORP values for the Westminster raw water, the utility correlated color with ORP mV levels. The permanganate dose yielding a 700 mV ORP reading also created pink water, indicating an overdose of  $\text{KMnO}_4$ . As a result, the initial work started with an ORP set point just below 700 mV. Since there will always be variables other than  $\text{Mn}^{2+}$  concentration driving the oxidant demand, finding a range of appropriate ORP readings was important. Through trial and error, the City established the current target ORP reading between 500 and 600 mV with a band of ORP values of  $\pm 50$ -75 mV.

The ORP instrument samples water downstream of permanganate addition but before the addition of any other chemical. Sample streams should have a relatively high turnover rate at the sampling location so that the ORP result remains current. Westminster has found that providing 2 minutes of contact time between the permanganate addition and the ORP sample provides a fairly stable result. This extra contact time can be accomplished by extra loops in tubing

between the sample tap and the instrument, if needed. The installed ORP probe is shown in Figure 7.2.



**Figure 7.2 ORP sensor installed**

The proportional-integral-derivative (PID) setup includes an inverse control loop which varies the  $\text{MnO}_4^-$  dosage inversely to the ORP reading, with a site specific set point. The process loop uses a reset rate of up to 2 hours which is related to the process timing (travel time for the chemical from the permanganate feed room to the dose point and travel time for plant flow to the measurement point) with a multiplier to avoid cyclical “hunting” by the feedback loop. The query time for the feedback loop in winter ranges from 15 to 30 minutes. The system has both a high (0.3 mg/L) and low (0.06 mg/L) range of output variables for the permanganate dose so that during seasonal peaks a high range can be used, while in the off-season very low doses of permanganate are possible. Westminster found that an instantaneous dosage change produced better treated water results, so Westminster recommends feeding a neat chemical solution (no carrier water), if possible. Example raw water ORP trends and permanganate dose trends are shown in Figure 7.3.

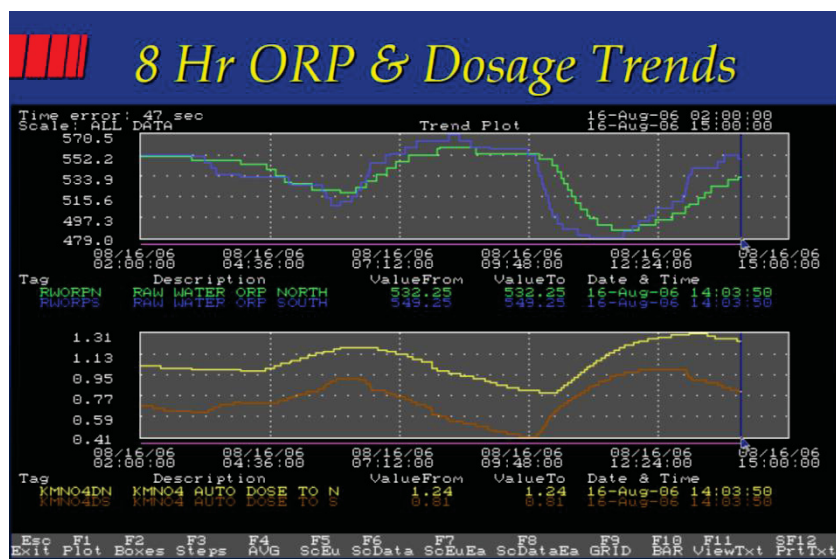


Figure 7.3 ORP and dosage trends from SCADA

### Operation and Maintenance of ORP Control

Critical to the use of an ORP instrument is daily maintenance of the probes. Westminster personnel clean the probes using water (no harsh chemicals) and a toothbrush as shown in Figure 7.4. To buy-in to using this approach to Mn control, the operational staff had to understand the process chemistry and see the successful removal of Mn in the treatment plant. Some education in the control parameters, dosage band, mV set point and reset rate was necessary for staff members.



Figure 7.4 Daily cleaning the ORP probe

### Results

The water quality objective at the plants for Mn is now < 0.01 mg/L of total Mn in the finished water. The plants meet this target 90% of the time, with 95% of total Mn readings < 0.02 mg/L. In the conventional treatment plant, finished water turbidity levels have been reduced since the ORP control was brought on line and filter run times in both the conventional and membrane plant have increased. Post-membrane turbidity issues that had been occurring



due to  $\text{Mn}^{2+}$  oxidation in the clearwell with free chlorine have been eliminated. Chlorine demand and ammonia usage have been reduced since the ORP control operation began and the consistency of the chloramine residual has improved.

Westminster has found that the old flow-paced controls for permanganate resulted in highly variable oxidation results, while the ORP approach provides a means of controlling finished water Mn at finite levels. Westminster has seen improvements in many elements of treatment, including chlorine residual management, turbidity and filter operations. The plants now maintain a constant oxidation potential (as measured in mV) by dosing the correct amount of oxidant to meet the existing demand. Recently, use of very small doses of permanganate to maintain target ORP settings during the early spring has shown that the permanganate can eliminate taste and odor compounds arising from a small algae bloom.

The methods were originally developed using  $\text{KMnO}_4$  at both facilities. Westminster has now switched to using 20% sodium permanganate at the conventional plant, with no significant change to the control process. The plant staff recommends consideration of  $\text{NaMnO}_4$ , but advises to not use PVC piping products for supply and feed lines. Over time, all injection-molded PVC components (elbow, tee, etc.) have developed pinhole leaks. Westminster has converted all of the  $\text{NaMnO}_4$  supply lines to stainless steel and feed lines to nylon tubing, using peristaltic pumps for dosing the chemical in neat form to the injection point.

## **CITY OF CHEYENNE, WY, BOARD OF PUBLIC UTILITIES**

**Problem:** Lake stratification in the summer releasing Mn at levels that were not treatable with the existing plant.

**Solution:** Use of hypolimnetic aeration supplied from a liquid oxygen system in the terminal reservoir.

### ***Background***

In August 2006, the Board of Public Utilities (BOPU) experienced a colored water event lasting approximately three weeks. The source of this event was Mn released from sediments of Crystal Lake under anoxic conditions and conveyed in the raw water supply to the RL Sherard Water Treatment Plant (WTP). Despite all efforts by BOPU staff, the Sherard WTP was unable to oxidize and remove enough Mn to prevent colored water complaints by BOPU customers. Customer complaints were received from customers throughout the distribution system.

During the three-week event, raw water Mn concentrations of up to 2 mg/L were observed and dissolved Mn concentrations exiting the plant at times exceeded 0.3 mg/L. Elevated dissolved iron concentrations were also assumed to be present in the raw water from Crystal Lake, but the iron was effectively treated. Ultimately, the Mn event ended when sufficient oxygenated water from upstream reservoirs was supplied to Crystal Lake, thereby reducing raw water Mn concentrations in the Sherard WTP supply to treatable levels. Throughout the colored water event, sufficient disinfectant residual was maintained in the distribution system and no adverse health effects were noted.

### ***Source Water Supply System***

BOPU operates a diversified raw water collection system supplied by both surface and ground water sources. Approximately 25 percent of the BOPU treated water supply is ground water and 75 percent is surface water. Raw water quality data from the ground water sources indicated that the Mn problem was related to the Crystal Lake source and not ground water supplies.

Four reservoirs store the surface water supply – Rob Roy and Lake Owen in the Medicine Bow Mountains and Granite Springs and Crystal Lake in the Laramie Mountains. Crystal Lake is the terminal reservoir supplying the Sherard WTP with raw water via two pipelines. A schematic diagram of the source water supply system is shown in [Figure 7.5](#).

Operation of the source water supply system is based on a number of requirements including optimizing water rights, taking facilities out of service to meet maintenance or construction needs and managing water quality impacts to the Sherard WTP. Management of the upstream reservoirs and the water quality in those reservoirs can have an impact on water quality at the Sherard WTP. Based on the operational experience of the Sherard WTP staff, the approximate flow travel time from the lake inlets through Crystal Lake and the raw water pipeline to the water treatment plant is 21 days. This estimate is based on the time it takes for water quality changes measured at the inlet to Crystal Lake, particularly DO and temperature, to appear at the Sherard WTP.

### ***R.L. Sherard Water Treatment Plant***

The Sherard WTP is a relatively new, state-of-the-art plant designed to meet disinfection byproduct (DBP) targets of 40 micrograms per liter ( $\mu\text{g/L}$ ) for TTHMs and 30  $\mu\text{g/L}$  for HAA5. As conceived, the plant was to operate as an ozone plant with biologically active filters. However, the plant is operated as a conventional treatment plant, bypassing the ozone treatment process. Ozone has not been operated because the continual feed of chlorine to the filter influent to foster Mn oxidation in the filters precluded the opportunity to operate biologically active filters to remove biologically degradable organic carbon downstream of ozonation. The plant's treatment train consists of pressure reduction (with the ability to add chlorine dioxide at this point), chemical addition (ferric sulfate with soda ash and catfloc polymer), static mixing, flocculation, sedimentation with lamella plates and filtration using dual media anthracite/sand filters. At the time of the colored water event, a nonionic polymer and chlorine were added to the filters to improve filterability and inhibit dissolution of Mn precipitated on the filters. Disinfection credit and distribution system residual are maintained with free chlorine. Soda ash is used to adjust treated water pH and fluoride is added as a public health benefit. Permanganate addition at the pressure reducing valve (PRV) vault at the plant and later at Crystal Lake outlet was used on a temporary basis during the colored water event.

The primary treatment challenge is TOC removal in low alkalinity water. The 2006 colored water event also demonstrated that the plant is challenged by high dissolved Mn levels. The current plant treatment capacity is 35 million gallons per day (mgd), expandable to 55 mgd. A schematic drawing of the plant processes and chemical feed locations is shown in [Figure 7.6](#).

### ***Treatment During Manganese Event***

The Sherard WTP staff utilized, in various combinations, all the oxidation power they had at their disposal during the 2006 event. Typically, Mn was controlled under normal circumstances by oxidizing at the PRV vault at the plant intake using chlorine dioxide. Chlorine was normally fed into the filters to maintain Mn removal in the filters through adsorption. At various points during the 2006 event, the combinations of oxidizers used for Mn oxidation included: chlorine dioxide with chlorine; intermediate ozone; chlorine dioxide, ozone and permanganate (fed either at the reservoir outlet or at an intermediate vault about half-way down the 14-mile raw water pipeline). Ferric sulfate at doses of 35 to 49 mg/L and polymer doses of 1.7 to 4.4 mg/L were fed for coagulation. Of the oxidant combinations utilized, none were successful for removing Mn to low levels, as the graphs of event data illustrate.

The staff reported that during the period that ozone was operational, a scum developed on the top of the filters that had to be backwashed out, causing them to decide to stop ozonation. The plant typically recycles backwash water, but during the Mn event the recycle stream was turned off.

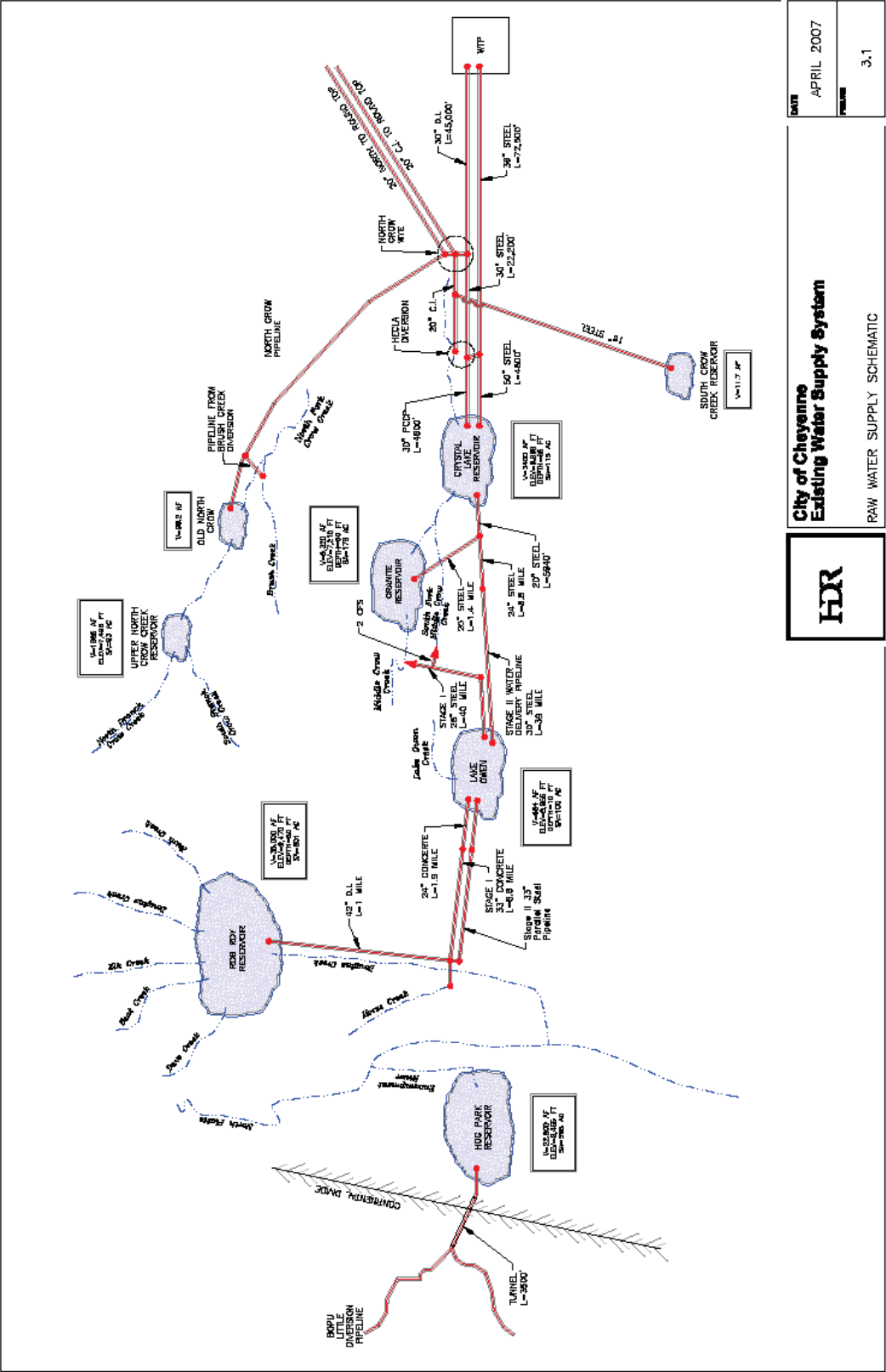


Figure 7.5 Schematic diagram of source water supply system for BOPU

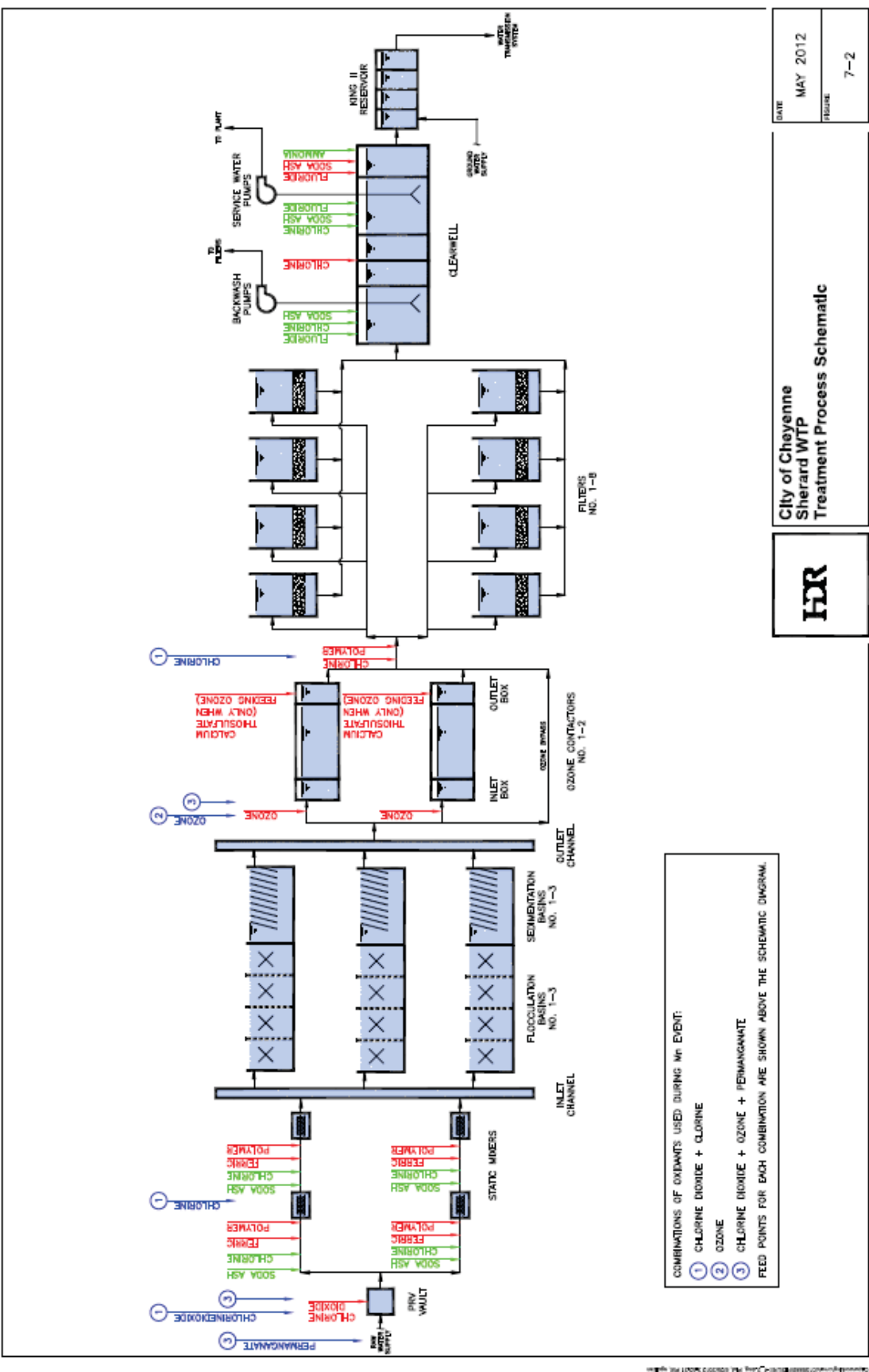


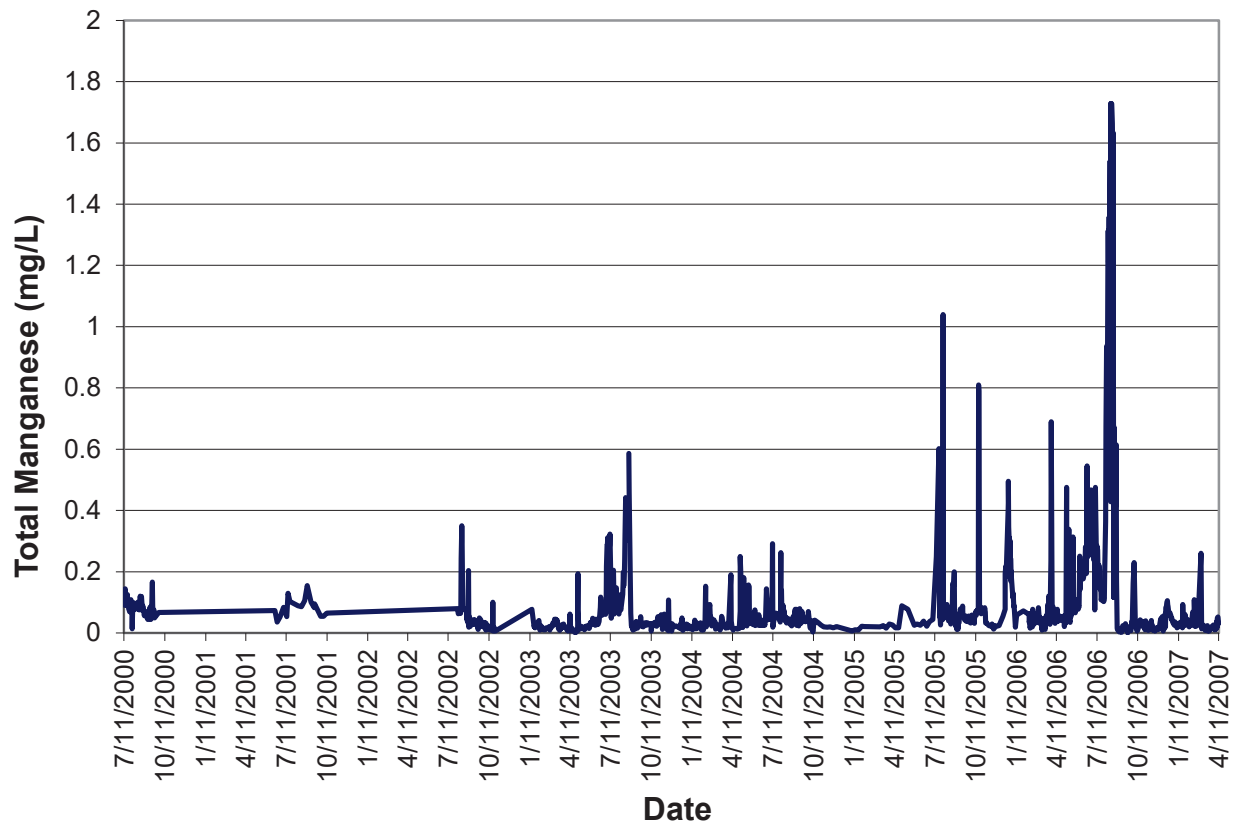
Figure 7.6 R.L. Sherard WTP treatment processes



### *Historic Manganese Conditions*

Since Crystal Lake is the terminal reservoir and direct source of raw water for the WTP, its behavior is critical with respect to Mn and iron release, as well as biological activity. Crystal Lake stratifies each year in late summer with respect to temperature and DO content (see [Figure 3.4](#)). Historically, the stratification appears to be stronger when flows from upstream reservoirs in late summer are low or none, which indicates that upstream supplies likely retain higher oxygen through the summer. While data are not available to confirm the correlation between upstream influent flows and Mn events, the anecdotal evidence from experienced operating staff supports the relationship.

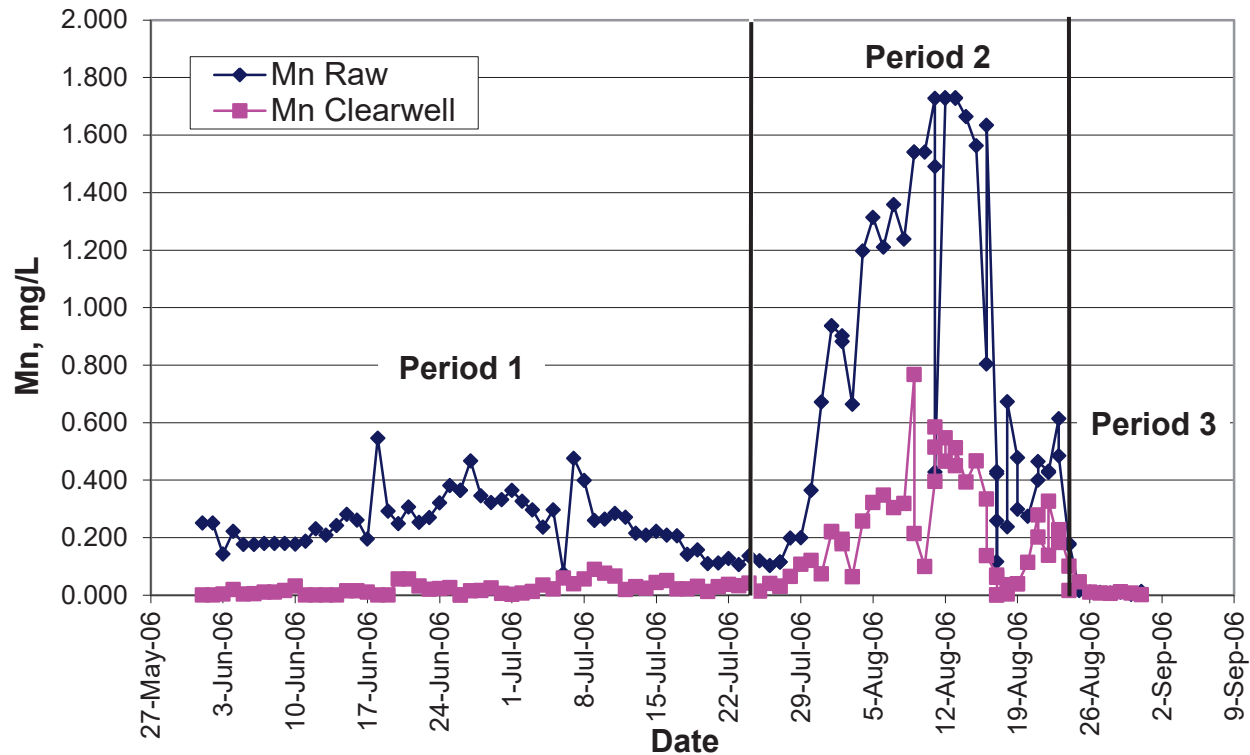
Based on the raw water Mn levels shown in [Figure 7.7](#), elevated Mn regularly occurs in late summer (July) in Crystal Lake. This increase of Mn in the raw water supply is correlated with the time of year that the DO decreases to near zero.



**Figure 7.7 Historical raw water manganese in Crystal Lake**

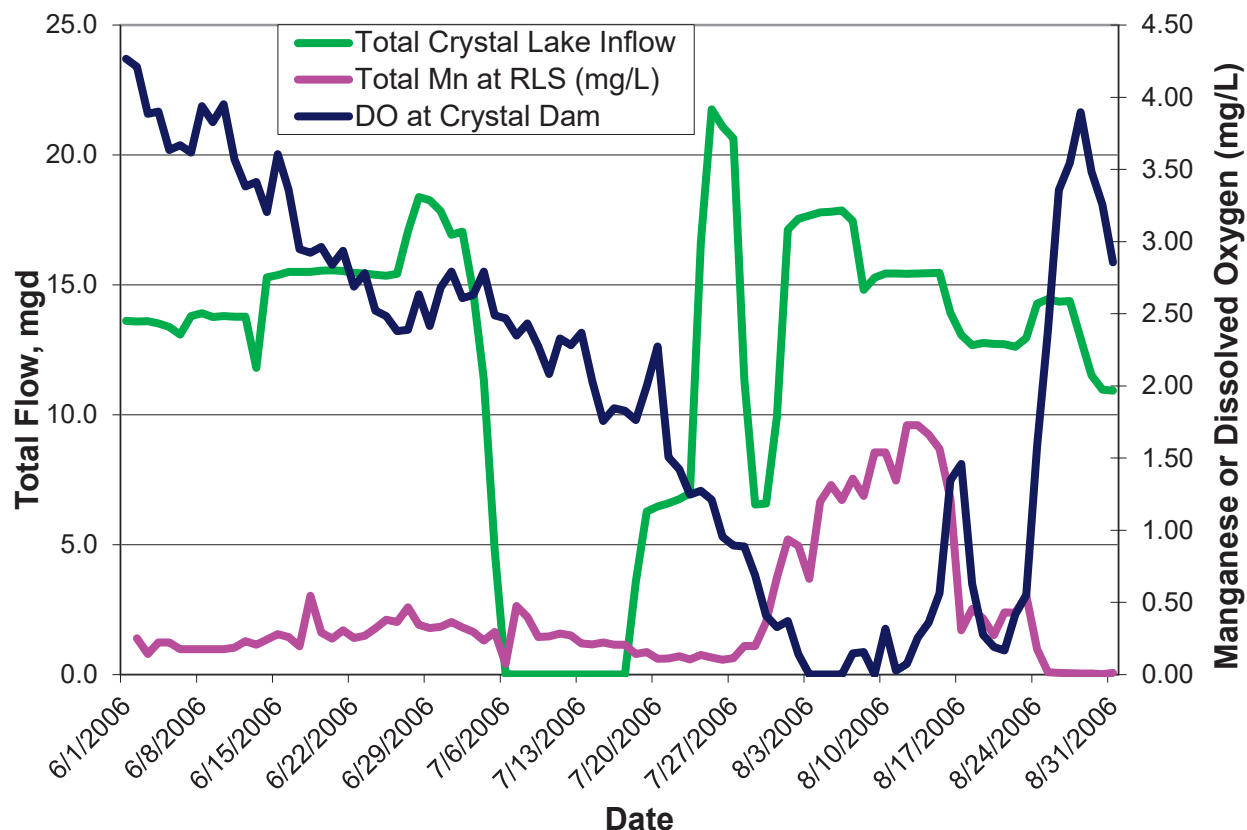
The Mn data over the summer of 2006 shown in [Figure 7.8](#) indicate that at the beginning of the summer there were low levels of Mn entering the Sherard WTP that were controlled by the treatment process (Period 1). In late July, a significant spike in Mn signaled the beginning of a major event (Period 2). By late August, the Mn entering the plant dropped to very low levels and the event ended (Period 3). By analyzing the data in these three time periods as separate groups of information, an understanding of what was happening and what was working to control Mn in

Periods 1 and 3 could be compared to the events during Period 2 when the Mn levels were not controlled.



**Figure 7.8 Raw and finished water manganese during summer 2006**

As is evident from [Figure 7.9](#), the flow into Crystal Lake was stopped in early July. Within about 21 days (the estimated travel time across the lake from the inlet to the outlet) the DO level became depleted and the raw water Mn level began to climb. The measured level of Mn at the WTP was actually higher than at the outlet from Crystal Lake due to additional dissolution of Mn from the 14-mile pipeline from the reservoir to the plant intake. After the influent flow was resumed from upstream sources, the DO began to climb at the reservoir outlet (same estimated 21-day delay is evident) and the Mn decreased at the plant intake. The situation that occurred in Cheyenne is an excellent example of the increase in Mn as a result of seasonal depletion of oxygen in the hypolimnetic layer of the terminal reservoir.



**Figure 7.9 Flow into Crystal Lake, dissolved oxygen at Crystal Dam and manganese at Sherard WTP**

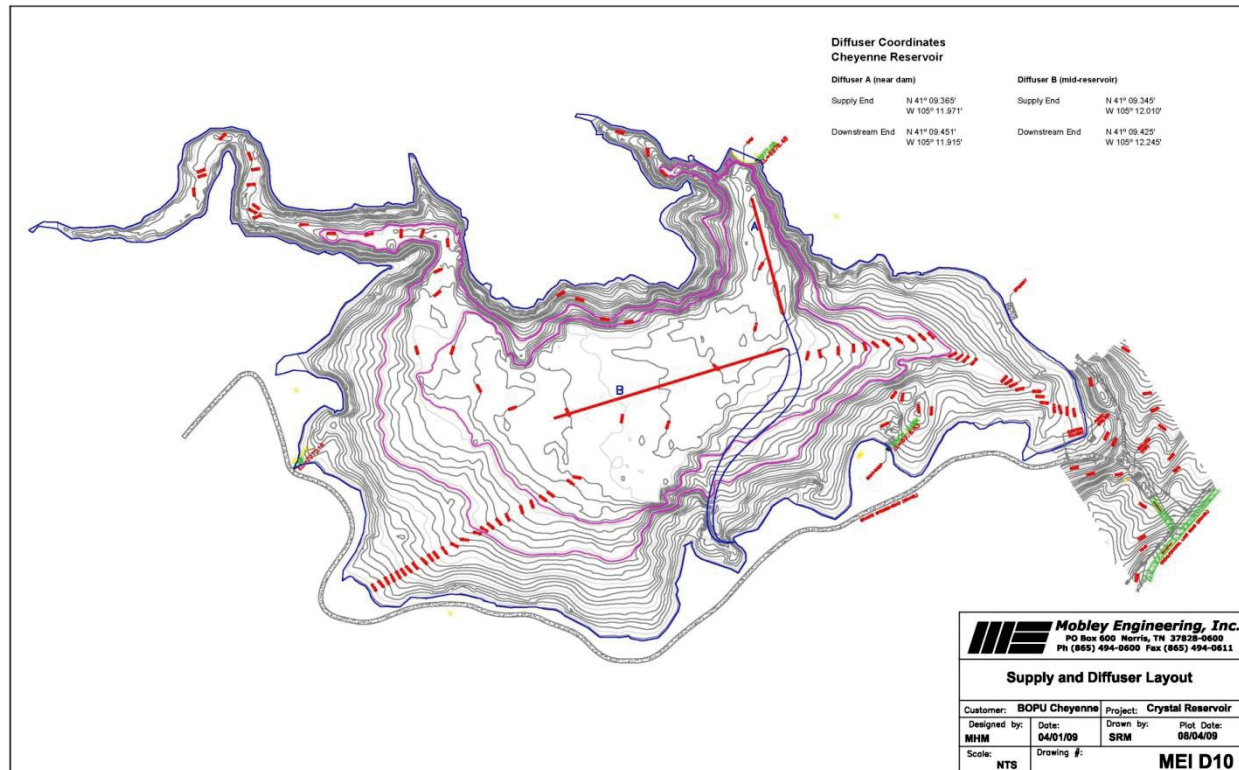
### *Solving the Manganese Problem in Cheyenne*

The Cheyenne BOPU considered a number of alternatives for managing Mn spikes in their water supply, with the objective of never having another event similar to the one that occurred in 2006. Two major approaches were developed:

- Design and construct a permanganate feed facility that would dose permanganate into the raw water pipeline a short distance outside the plant to provide adequate contact time for oxidation of Mn prior to the addition of coagulant at the rapid mix.
- Install aeration in the hypolimnetic layer of Crystal Lake Reservoir to minimize the dissolved Mn leaving the reservoir and providing adequate oxygen in the water to keep the Mn deposits in the 14-mile raw water pipeline in place (prevent solubilization of Mn along the pipeline). This system controls dissolved Mn by eliminating dissolution of Mn from sediment and biological substrate, not by oxidizing Mn.

Of these two approaches, the permanganate feed system was completely designed but not constructed as the cost was significant. Instead, an aeration system for the reservoir was designed and installed. The aeration system at Crystal Lake is a liquid oxygen (LOX) system that feeds gaseous oxygen into two long diffuser lines that are positioned in the bottom of the reservoir in specific locations developed through modeling. The LOX system is located in a

small enclosure on the hillside above the lake, which is part of a state park. Oxygen feed lines to the lake are buried and enter the lake at a single location, as shown in [Figure 7.10](#).



**Figure 7.10 LOX diffuser layout for Crystal Lake Reservoir, City of Cheyenne**

The oxygen delivered to the water is in the form of a bubble plume through a supply line with diffuser hoses attached to it. The supply lines are paralleled in the lake by a buoyancy pipeline which allows the whole system to be floated and sunk as a unit by filling the buoyancy pipeline with either water or air as shown in [Figure 7.11](#).

The system is operated from April to October, with oxygen flows at a very low level early in the season and slightly higher later in the summer. Since the system was started in spring 2009, the DO concentrations have remained well above the approximate 5 mg/L that experience has shown will minimize Mn in the raw water supply at the Sherard WTP. When the system is on, the oxygen concentrations at the plant shift within 48 hours of a feed adjustment. The amount of oxygen being fed ranges from 2.5 to 15 standard cubic foot per minute (scfm). Once the water in the hypolimnion is oxygenated, a feed flow in the range of 2.5 to 3 scfm is adequate to maintain oxygen levels through the summer months.

[Figure 7.12](#) shows the DO levels at the plant from 2008 through the 2010 LOX operating season and [Figure 7.13](#) shows the Mn levels in the raw water at the plant since the aeration system has been on line. Comparing the current Mn levels with those experienced in 2006, where the high level reached nearly 2 mg/L, illustrates the effectiveness of the aeration system in preventing dissolved Mn from forming.

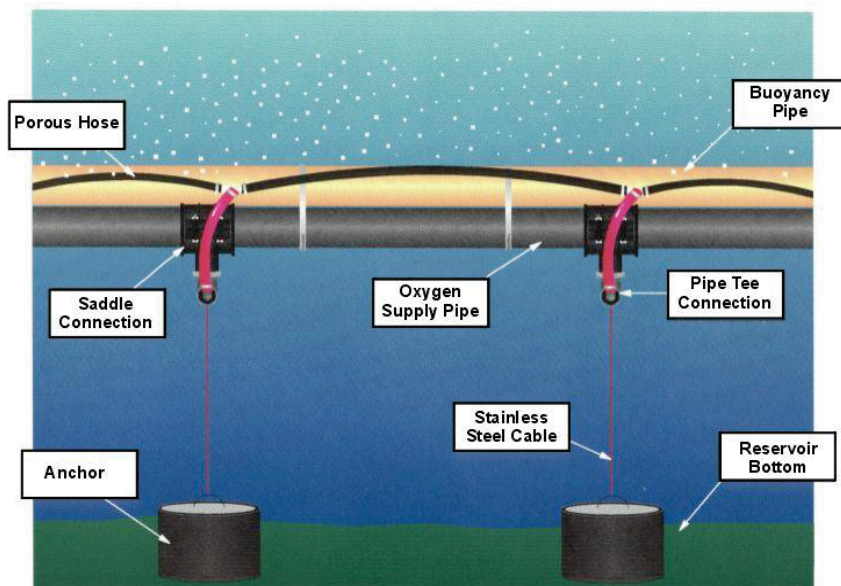


Figure 7.11 In-lake oxygen supply system utilized at Crystal Lake

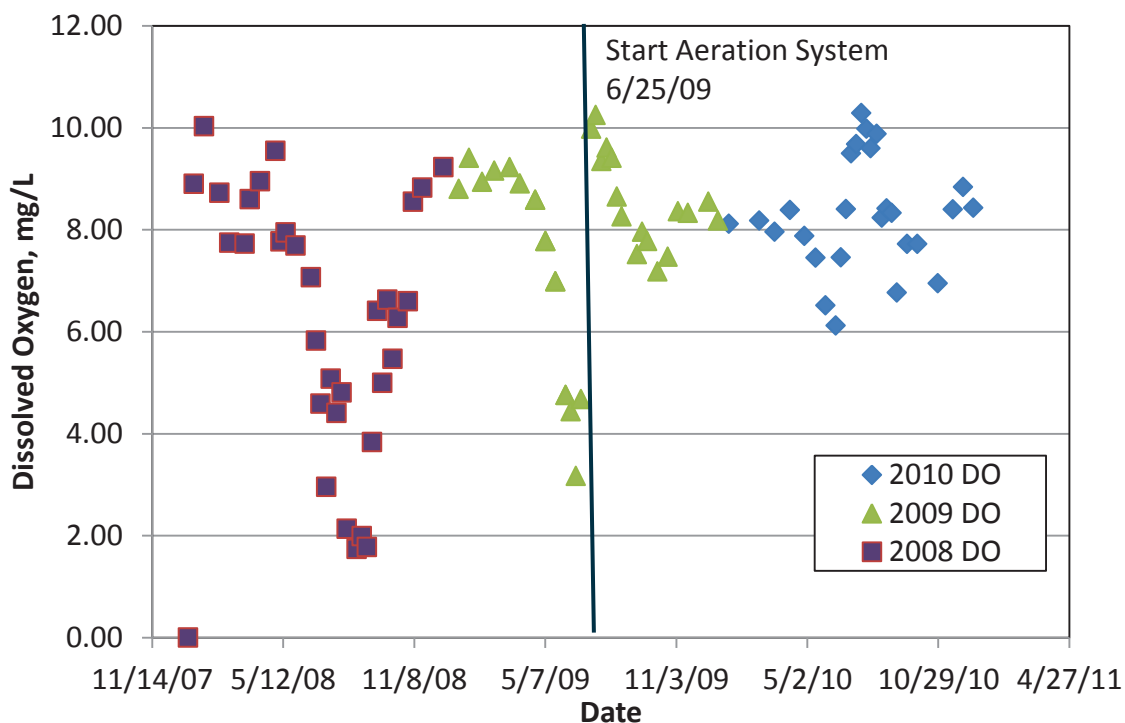
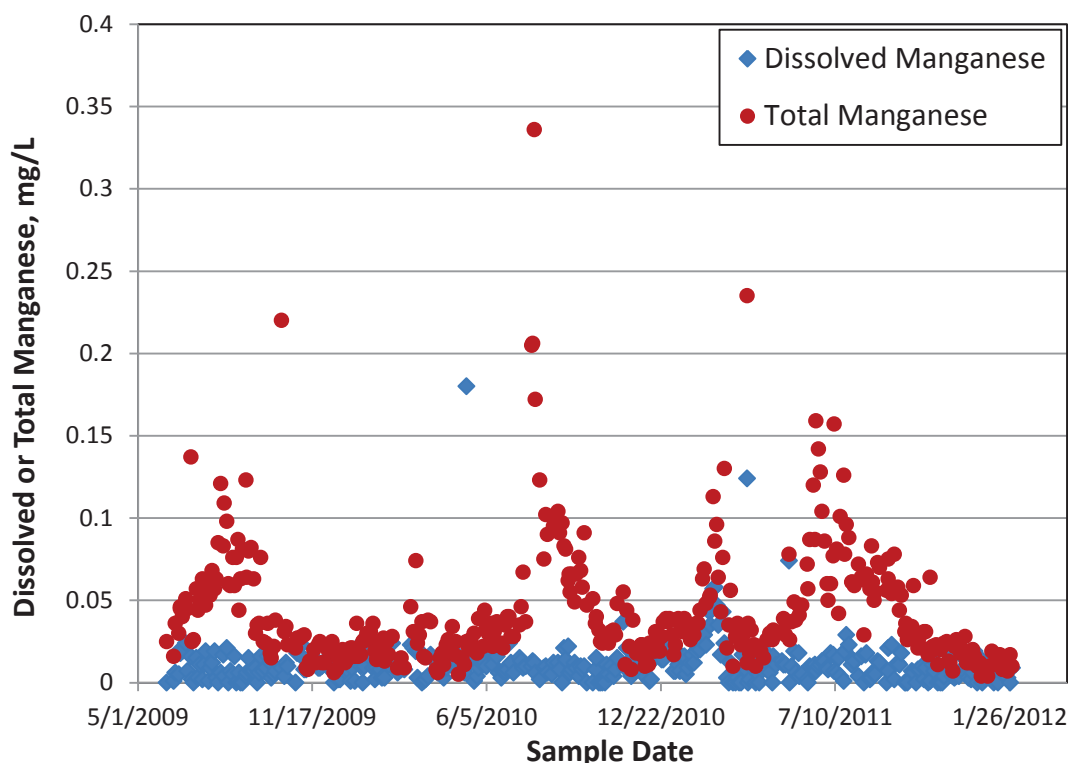


Figure 7.12 Dissolved oxygen at Sherard WTP intake (raw water at the plant)





**Figure 7.13 Raw water total manganese at the Sherard WTP after installation of hypolimnetic aeration at Crystal Lake Reservoir**

### ***Results***

The result of applying gaseous oxygen into the bottom of Crystal Lake is that the Sherard WTP now has very little dissolved Mn in their raw water at the plant and the plant has eliminated chlorine dioxide feed at the head of the plant. The utility reports that their experience with the aeration system installation and operation has all been positive – Mn is reduced to near zero, overall chemical costs are reduced, sludge volume is reduced and may be reduced further with the option of testing alternative coagulants. No negative issues have arisen.

Aeration lessons learned. The utility elected to purchase the LOX tank rather than lease it, allowing them to bid the LOX as a chemical product and reduce chemical costs. By establishing a 3-year supply contract, the utility was able to lower the price of LOX from \$0.50 to \$0.30/100 cf. The system itself is reportedly “hassle free” with minor checking once a week while it is operating.

Filter cleaning. Historically, chlorine was fed to the filter influent to ensure that residual Mn would oxidize onto the filter media. Plant staff report that when the chlorine feed was turned off, Mn dissolved off the filter media and appeared in the clearwell within a day. With raw water Mn levels reduced to near zero, the plant wanted to stop feeding chlorine to the filter influent. Cheyenne were concerned that with the chlorine feed off, Mn would be dissolved off the filter

media and filter basin walls. As a result, an effort was undertaken to clean the filter bays and filter media by soaking them in sodium bisulfite. The process was successful, so the plant has eliminated the chlorine feed to the filters. A direct benefit of stopping the chlorine feed is that Cheyenne has seen a reduction in disinfection byproducts. Filters appear to recover more quickly after backwashing, although Cheyenne did find that it took approximately 4 to 5 weeks of operation before the cleaned filters stopped releasing Mn.

The following is a description of the process used by the utility to clean the filters.

A plant filter is 24' x 32'6"; Design parameters: five feet of anthracite media on top of one foot of sand, all supported by Leopold Type "S" filter underdrain blocks.

To begin, the operator backwashes and drains a filter. After backwashing, the operator allows the filter to drain until the effluent meter reads less than 100 gpm or 10-15 minutes, whichever comes first. The filter is isolated (close all of valves - inlet, filter to waste, effluent to clearwell, air scour and drain). The operator cores and collects media samples from four spots in each filter, as well as measures the depth of media for future reference.

The operator(s) plumbed-in to the filter box a removable 3" schedule 80 PVC pipe to allow the transport vehicle to connect their discharge hose and off-load sodium bisulfite solution. The operators place a piece of plywood on top of the media to keep from scouring the media surface with flows from the piping discharge. The tanker vehicles off-load 6,000 gallons of sodium bisulfite, 40% solution into a filter. The tanker trucks pump and/or flow by gravity their product onto the filter. After unloading, the operator pulls the plywood and piping out of the filter box and brings the water level to about four inches above the media. The operator initiates an air scour and mixes the media up to 2 minutes. Let soak for 2 hours.

The operator raises the water level to the bottom of the backwash troughs and air scours until the foam (created by air scour) overflows the backwash troughs. The operator secures the air scour blower and raises the water level to a point just above "normal operating range". The product also cleans the filter walls, thereby removing black staining from the walls and troughs. The product has minimal impact on iron staining (ferric sulfate coagulant). Hold the water level for another 2 hours and backwash to waste. After two or three backwashes, the operator filters to waste until the Mn concentration in the filtered water is at or below 0.05 mg/L and places the filter in service; anywhere from 20 to 24 hours.

Despite Cheyenne's success, it should be noted that filter cleaning may not be technically or economically feasible in all cases. The suitability of filter cleaning will be site specific and depend on specific circumstances faced by a utility (number of filters, filter design, backwash disposal options, filter to waste options, cleaning chemical costs, chemical disposal costs to name a few). In a later case study (MWDSC) filter cleaning was evaluated and rejected as an option to eliminate Mn bleed from filters after a chlorine feed was eliminated from the filter influent.

## NEWPORT NEWS, VA

**Problem:** Reservoir water sources contain variable Mn concentrations, with seasonal spikes. Two treatment facilities employ different Mn treatment approaches. Also, Mn-laden waters from residuals handling systems can create a substantial load of Mn to treatment systems due to water reclamation efforts.

**Solution:** Treatment plants use specific control techniques that are integrated into overall treatment objectives; also, dissolved Mn removal for waters originating from residuals handling systems are effectively treated using  $\text{MnO}_x(\text{s})$ -coated filtration media.

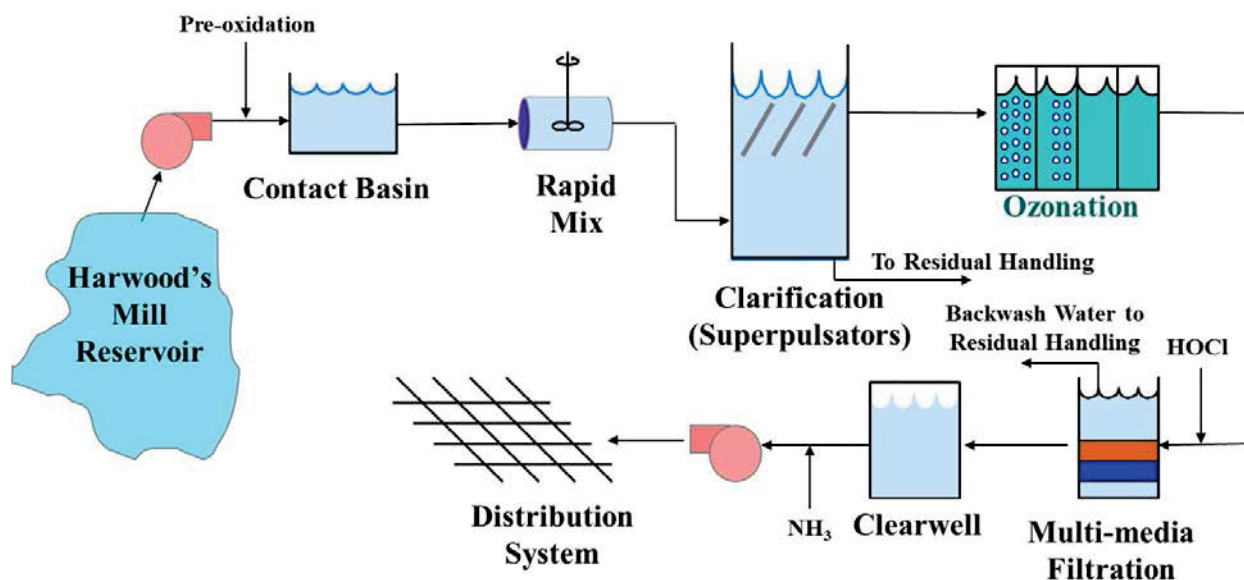
### *Manganese Removal Operations Within the Newport News Waterworks Facilities*

The City of Newport News has an extensive water supply system and furnishes water to the lower Virginia Peninsula including the cities of Newport News, Hampton and Poquoson and portions of James City and York Counties. Newport News Department of Public Utilities, hereafter referred to as Waterworks, owns and operates the entire water system, selling finished water directly to its customers in Newport News, the other political subdivisions and to certain secondary systems. In addition to supplying finished water, Waterworks can supply raw water to the City of Williamsburg.

The primary raw water source for the Waterworks is the Chickahominy River. Through a combination of river water and reservoirs the Waterworks employs two terminal reservoirs to supply water to its two major water treatment facilities (described below). The Lee Hall Water Treatment Plant is supplied from the Lee Hall Reservoir, which has a surface area of 493 acres and a rated storage capacity of 850 million gallons. The Harwood's Mill Water Treatment Plant is supplied from the Harwood's Mill Reservoir, which has a surface area of 265 acres and a rated storage capacity of 912 million gallons. Hence, on average the Harwood's Mill Reservoir is significantly deeper than the Lee Hall Reservoir. Both terminal reservoirs undergo stratification at times during the year, with resulting elevated concentrations of soluble Mn in the water from the hypolimnetic region of each reservoir. Waterworks personnel undertake a substantial water quality monitoring program on both reservoirs to aid in treatment process decision making.

Water quality in the Chickahominy River (which is characteristic of water quality in both terminal reservoirs) is reflective of a relatively low hardness (30-40 mg/L as  $\text{CaCO}_3$ ), low to moderate alkalinity (30-60 mg/L as  $\text{CaCO}_3$ ), organic-laden (average annual raw water TOC for both reservoirs between 7-7.5 mg/L) surface water. Typical pH values fall between 7.0 to 7.7 in both reservoirs.

The Harwood's Mill water treatment plant (completed in 1989) has a plant capacity of 31 MGD, with capability to expand to 52 MGD at a later date. The Harwood's Mill plant, which takes water from the terminal Harwood's Mill Reservoir, utilizes the unit operations of screening, raw water pumping, flow measurement, preoxidation/reaction, flash mixing/coagulation, ultra-high rate clarification (Superpulsators), high rate filtration, post-treatment and finished water storage. A schematic of the treatment facility is shown in [Figure 7.14](#). Typical chemical feeds during treatment include potassium permanganate, alum, coagulant aid polymer, sulfuric acid, ozone, sodium hypochlorite, ammonia, fluoride, lime and corrosion inhibitor (typically zinc orthophosphate).



**Figure 7.14 Schematic of the Harwood's Mill Water Treatment Facility**

The Lee Hall Water Treatment Plant (completed in 2003) has a rated surface water capacity of 54 MGD. The plant is quite similar to that of the Harwood's Mill treatment facility. Specific treatment steps include a raw water intake structure, a low lift pumping station, chemical contact basin, a two-stage chemical flash mixing basin, flocculation and dissolved air flotation (DAF) basins, ozonation facilities, filtration units, chemical feed facilities, a clearwell with chemical mixing capabilities and a high lift pumping station. Typical chemical feeds during treatment include sodium permanganate, alum, coagulant aid polymer, caustic soda, sulfuric acid, ozone, sodium hypochlorite, ammonia, fluoride, lime and corrosion inhibitor (zinc orthophosphate).

As listed the chemical feeds used are very similar at the two facilities, but there is one major difference in treatment approach that relates to dissolved Mn control. Treatment at the Harwood's Mill plant includes the addition of free chlorine to the filter-applied water, resulting in the uptake of dissolved Mn across the filters and a substantial accumulation of  $\text{MnO}_x(\text{s})$  coating on the filter media which is kept in a chemically regenerated condition due to the presence of free chlorine. The presence of free chlorine across the Harwood's Mill dual-media filters promotes very effective dissolved Mn removal, but does greatly minimize the potential for biofilm accumulation and degradation of the biodegradable DOC generated by ozonation upstream of the filters. In comparison, the Lee Hall Water Treatment Plant does not add free chlorine to its filter-applied water. As a result, there is minimal if any uptake of dissolved Mn across their dual-media filters and no appreciable  $\text{MnO}_x(\text{s})$  accumulation on the media surface. However, biodegradation of DOC does occur across the Lee Hall filters, resulting in increased biostability of the finished water.

Another significant treatment difference between the two facilities relates to the permanganate feed systems that are being deployed. Both facilities have the capability to add permanganate to the raw water for addressing dissolved Mn oxidation needs. At Harwood's Mill that is done through the use of potassium permanganate and an associated feed system that

requires dissolution of solid  $\text{KMnO}_4$  into water and feeding of the resulting stock solution. While potassium permanganate has been historically fed at the Lee Hall Water Treatment Plant, pilot testing at the facility has resulted in a decision to pursue feeding sodium permanganate. Primary benefits foreseen include the ability to purchase the sodium permanganate in a liquid feed directly from the chemical supplier, eliminating the need for solid  $\text{KMnO}_4$  dissolution and the associated challenges with such feed systems that were observed on occasion at the facility. Plant personnel have designed the full-scale feed system to utilize a 20%  $\text{NaMnO}_4$  solution given concerns about higher levels of corrosivity that may be associated with use of a 40% strength solution. Sodium permanganate does have a much higher unit chemical cost in comparison to  $\text{KMnO}_4$ . However, Lee Hall Water Treatment Plant personnel believe the intermittent feeding needs for permanganate during a typical year coupled with the perceived improvements in feed reliability and reduced O&M costs justify the change in permanganate feed source that is being made at this facility.

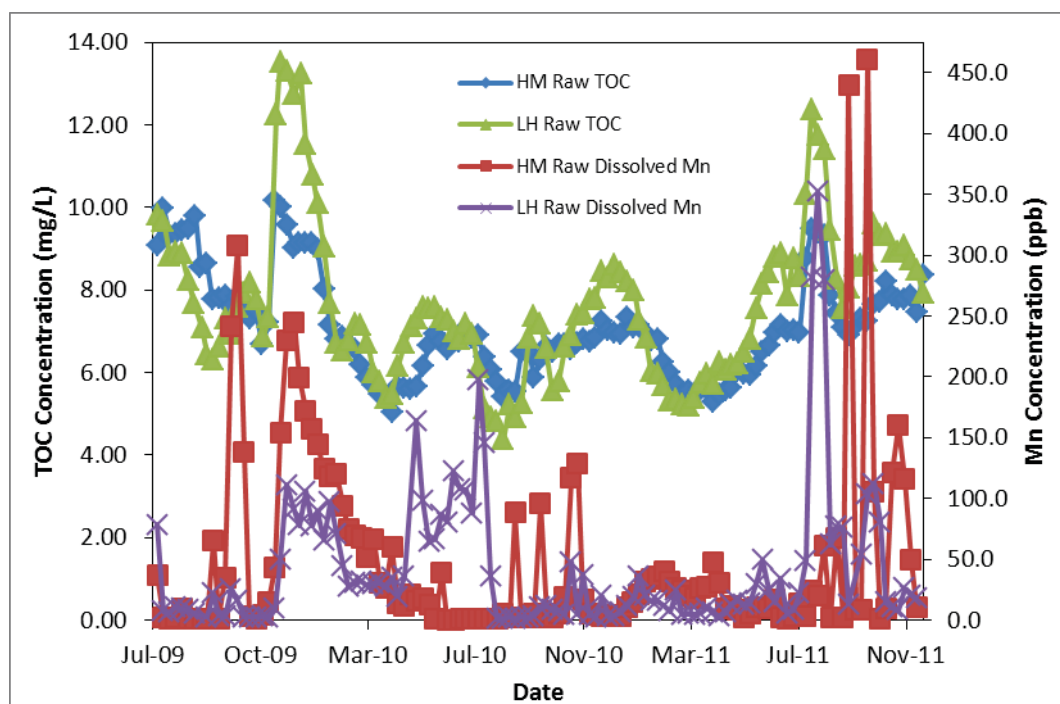
As mentioned previously the water sources to the two treatment facilities are fairly organic laden. Information regarding the raw water TOC level from each terminal reservoir feeding the treatment facilities as well as the finished water TOC is presented in [Table 7.1](#) for a recent three-year time period. Note that the vast majority of the raw water TOC (typically above 90%) was found to be in dissolved form (DOC). Given the typically high TOC values coupled with the relatively low raw water alkalinities of the sources the two facilities must routinely achieve 50% TOC reduction via treatment to comply with appropriate Enhanced Coagulation regulations. Data in [Table 7.1](#) indicate that both treatment facilities achieve on average TOC removals well in excess of that required by regulation.

An attempt was made to determine whether there was any substantial correlation between the raw water TOC levels in the terminal reservoirs and the levels of dissolved Mn present. [Figure 7.15](#) presents these parameters on a thirty-month historical basis for both parameters in both terminal reservoir sources. Perhaps as expected no strong correlation between raw water TOC and dissolved Mn levels was observed. Variations in raw water TOC levels (especially periods of elevated concentration) often were found to relate to precipitation events, whereas increases in dissolved Mn were more often due to stratification/destratification issues in the terminal water reservoirs. The uniqueness of each terminal reservoir with respect to elevated dissolved Mn concentrations can also be seen in [Figure 7.15](#). Note again that both terminal reservoirs are supplied almost completely from the same water source, the Chickahominy River.



**Table 7.1**  
**Raw and finished water TOC values for the two Newport News Water treatment facilities**

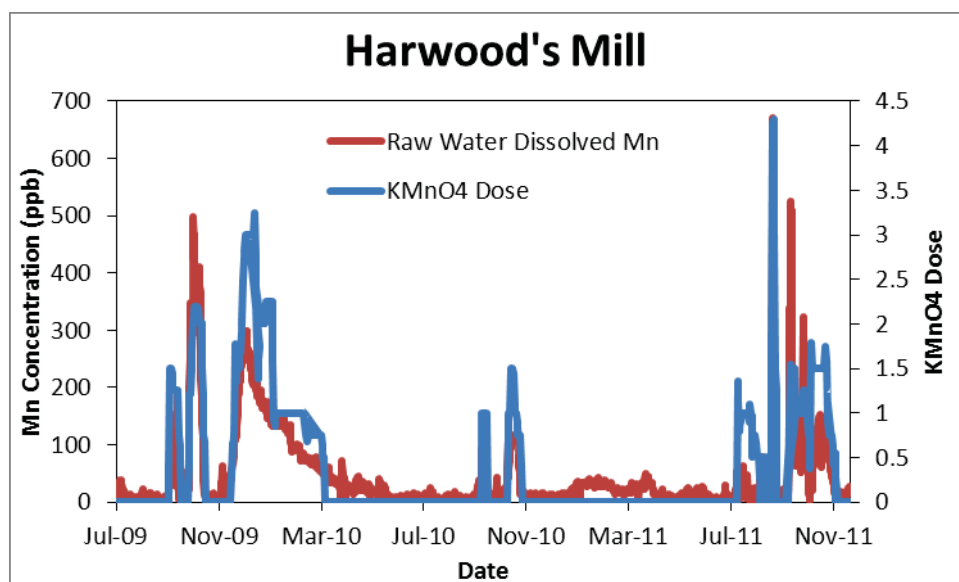
Year	Harwood's Mill		Lee Hall	
	Raw TOC (mg/L)	Finished TOC (mg/L)	Raw TOC (mg/L)	Finished TOC (mg/L)
2009	7.6 [5.0 - 10.2]	3.3 [2.7 - 4.5]	7.9 [4.7 - 13.5]	3.2 [2.5 - 4.1]
2010	6.5 [5.0 - 9.0]	3.0 [2.4 - 3.7]	6.9 [4.4 - 10.1]	3.0 [2.1 - 4.4]
2011	6.9 [5.3 - 9.5]	3.3 [2.8 - 4.1]	7.8 [5.2 - 12.4]	3.2 [2.5 - 4.2]



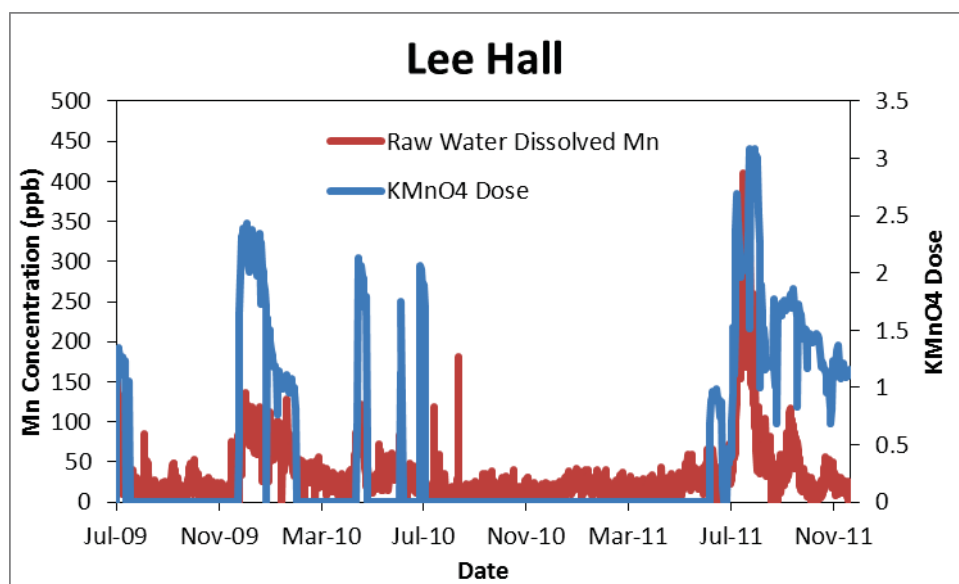
**Figure 7.15 Raw water TOC and dissolved Mn concentrations for the Lee Hall (LH) and Harwood's Mill (HM) terminal reservoirs over a thirty-month time period**

Historical data were reviewed regarding the permanganate dosage employed at each treatment facility in relation to raw water dissolved Mn concentrations; information for a thirty-month operational period are shown in [Figures 7.16](#) and [7.17](#) for the Harwood's Mill and Lee Hall treatment facilities respectively. As expected each facility often initiated permanganate dosing in response to situations involving substantial (e.g., greatly than 100 µg/L) levels of raw water dissolved Mn. Day-to-day permanganate dosages at both facilities could be highly variable (ranging from 0.2-3.2 mg/L at Harwood's Mill and 0.1-3.1 mg/L at Lee Hall); however, on average the permanganate dosage employed at Lee Hall was approximately 15-20% higher over the thirty-month time period, which may have been due in part to the slightly higher

average TOC values in the Lee Hall Reservoir water (since TOC is known to create a competitive oxidant demand for permanganate during Mn treatment by oxidation).



**Figure 7.16 Permanganate dosing patterns in relation to raw water dissolved Mn concentrations at the Harwood's Mill Water Treatment Facility**



**Figure 7.17 Permanganate dosing patterns in relation to raw water dissolved Mn concentrations at the Lee Hall Water Treatment Facility**

In addition to the employment of permanganate dosing as a pre-oxidant at each treatment facility, both also employed ozone addition after the solid-liquid separation step (either Superpulsator clarifiers at Harwood's Mill or dissolved air flotation separators at Lee Hall),

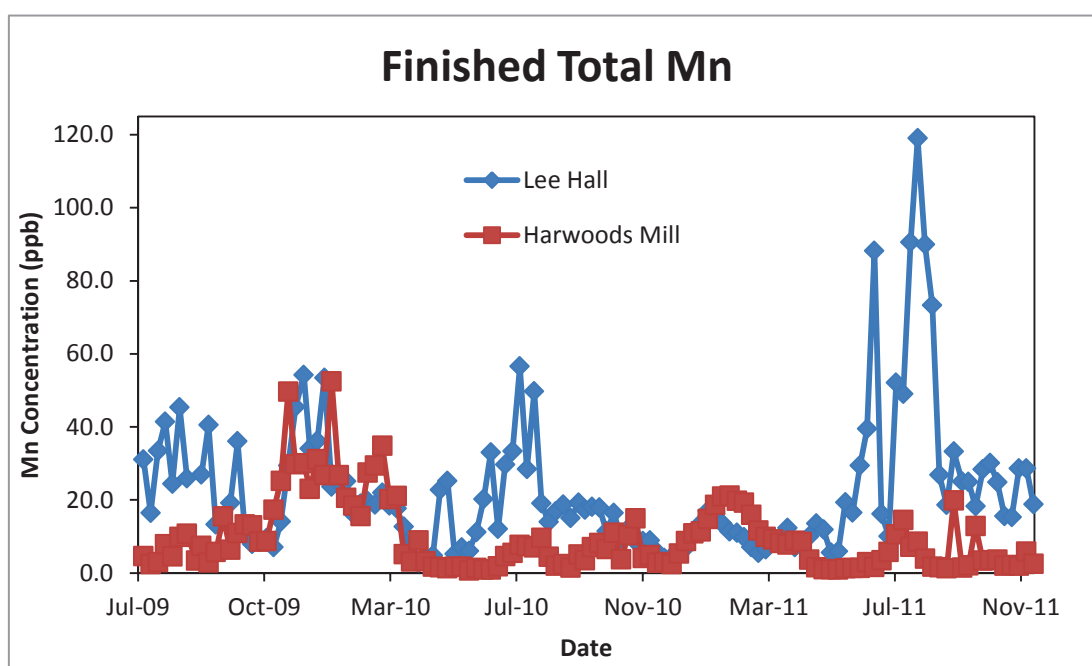
primarily for disinfection purposes. Although the data sets for dissolved Mn concentrations were limited as a function of locations along each treatment train, it was possible to draw certain inferences regarding the fate of dissolved Mn that entered the ozone treatment step. In general, minimal evidence of dissolved Mn oxidation was observed when the influent dissolved Mn concentration to the ozonator was at or below 40-50 µg/L. As such, ozone addition offered little oxidative benefit at either facility when these “nuisance” levels of dissolved Mn remained in the water at this stage of treatment. Evidence of significant dissolved Mn oxidation by ozone addition was normally seen when the dissolved Mn concentration entering the ozone treatment system was at or above 100 µg/L. In those instances the dissolved Mn concentration was typically lowered by reaction with ozone to a value near 40-50 µg/L. As such, two points are noteworthy. First, the addition of ozone did not achieve truly low (less than 20-30 µg/L) dissolved Mn concentrations after treatment. Second, when substantial (greater than 100 µg/L) dissolved Mn concentrations were present in the water applied to the ozone treatment system significant amounts of colloidal/particulate  $\text{MnO}_x(\text{s})$  formation was observed. Prior discussion in Chapter 6 noted that such colloidal or particulate  $\text{MnO}_x(\text{s})$  being formed just prior to the filtration step can create a need for a filter aid coagulant to be added to enhance the capture of these typically negatively charged solids within the filter itself. Otherwise, these solids may escape capture in the filter and contribute to the observed finished water Mn concentration.

Figure 7.18 presents comparative data over a thirty-month period related to the finished water Mn concentration leaving the Harwood’s Mill and Lee Hall water treatment facilities. A few observations regarding the data are noteworthy. First, both treatment facilities routinely achieve finished water Mn concentrations below the suggested secondary MCL of 0.05 mg/L, a standard felt to protect against consumer complaints associated with discolored water. Second, the benefit of having an  $\text{MnO}_x(\text{s})$ -coated filter media coupled with filter-applied free chlorine at the Harwood’s Mill facility is clearly evident in the data as the finished water Mn concentrations present were routinely below that produced from the Lee Hall facility (which does not have free chlorine present in front of  $\text{MnO}_x(\text{s})$ -coated filter media). This result was most notable during the warmer-month periods each year, when finished water Mn concentrations were often in the 20-40 µg/L range at Lee Hall but below 10 µg/L in the water produced at the Harwood’s Mill facility. Finally, the data indicate the possibility of a negative low temperature impact on dissolved Mn uptake onto  $\text{MnO}_x(\text{s})$ -coated filter media. During the winter periods of 2010 and 2011 the water temperatures at Harwood’s Mill were as low as 4-5 °C and often at or below 10°C. This coincided with periods of slightly higher Mn concentration in the finished water from this facility. While the data are anecdotal at this point the results do allow for the possibility that dissolved Mn uptake onto  $\text{MnO}_x(\text{s})$ -coated filter media may be negatively impacted by low water temperature conditions. The possible effects of temperature on this adsorptive Mn removal process have not been evaluated in the published literature since the winter months (with lowest water temperatures) are typically not a primary Mn removal season for surface water treatment facilities.

Discussions with Newport News Waterworks personnel led to an observation that there seemed to be a significant number of days during the year when the Lee Hall treatment facility actually produced water with greater amounts of Mn present in the finished water than was present as dissolved Mn in the raw water; in essence, cases of “net negative Mn removal overall” at the facility. A decision was made to more carefully evaluate the Mn removal results across both treatment facilities to see if such events were actually occurring. Fortunately Newport

News Waterworks has a well-designed and managed analytical protocol for evaluating Mn concentrations through both of its facilities, so ample data were available for this analysis. The raw water conditions for Mn concentration were subdivided into three bins for analysis:

- (a) Situations where both the total and dissolved Mn concentration in the raw water was below 0.05 mg/L;
- (b) Situations where the raw water dissolved Mn concentration was below 0.05 mg/L but the total Mn concentration was between 0.05 and 0.1 mg/L (indicating the presence of small amounts of oxidized, particulate Mn in the raw water); and,
- (c) Situations where the raw water dissolved Mn concentration was below 0.05 mg/L but the total Mn concentration was above 0.1 mg/L (indicating the presence of a substantial amount of oxidized, particulate Mn in the raw water).

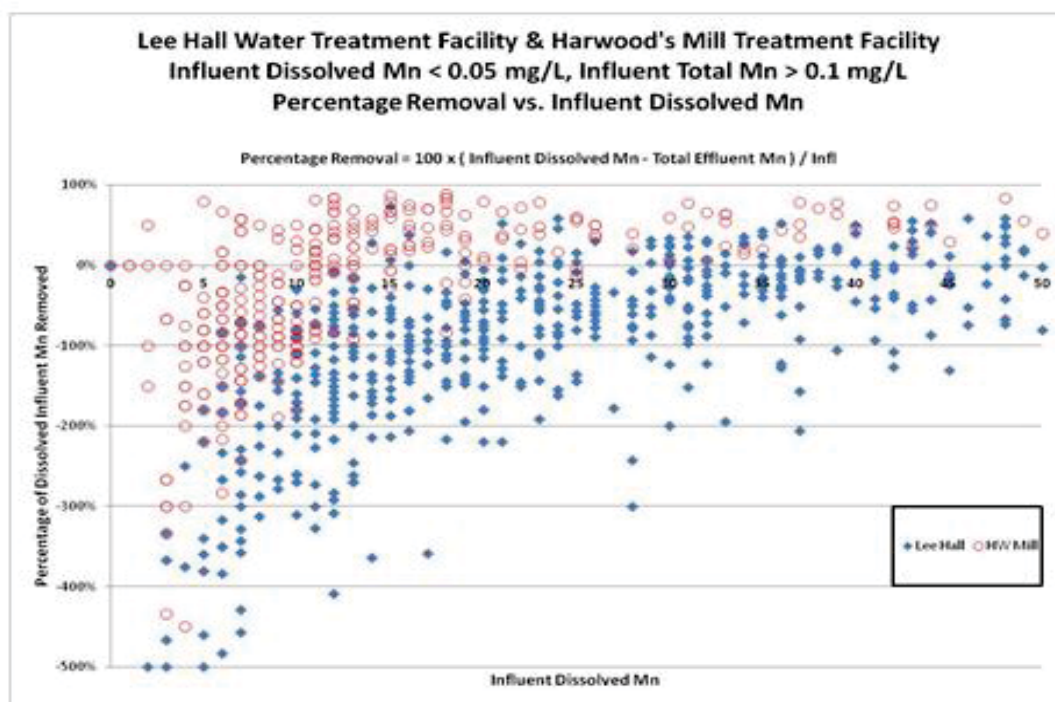


**Figure 7.18 Finished water Mn concentrations from the Harwood’s Mill and Lee Hall Water Treatment Facilities over a thirty-month period of operation**

In general, no substantial evidence of this situation (of higher Mn concentrations leaving the treatment facility than being present as dissolved Mn in the raw water) was seen for either facility when the raw water total Mn concentration was at or below 0.1 mg/L and the dissolved raw water Mn concentration was below 0.05 mg/L. However, interesting results were obtained when considering the third scenario described, namely when the raw water dissolved Mn concentration was below 0.05 mg/L but the total raw water Mn concentration was above 0.1 mg/L (again, indicating substantial amounts of oxidized, particulate Mn being present in the raw water). The performance of each treatment facility for overall dissolved Mn removal (calculated based upon consideration of the final Mn concentration leaving the facility in comparison to the dissolved Mn concentration entering in the raw water) when substantial particulate Mn was present in the raw waters is shown in Figure 7.19. Note that the data shown in Figure 7.19 include both instances when pre-oxidation with permanganate was being practiced and when no

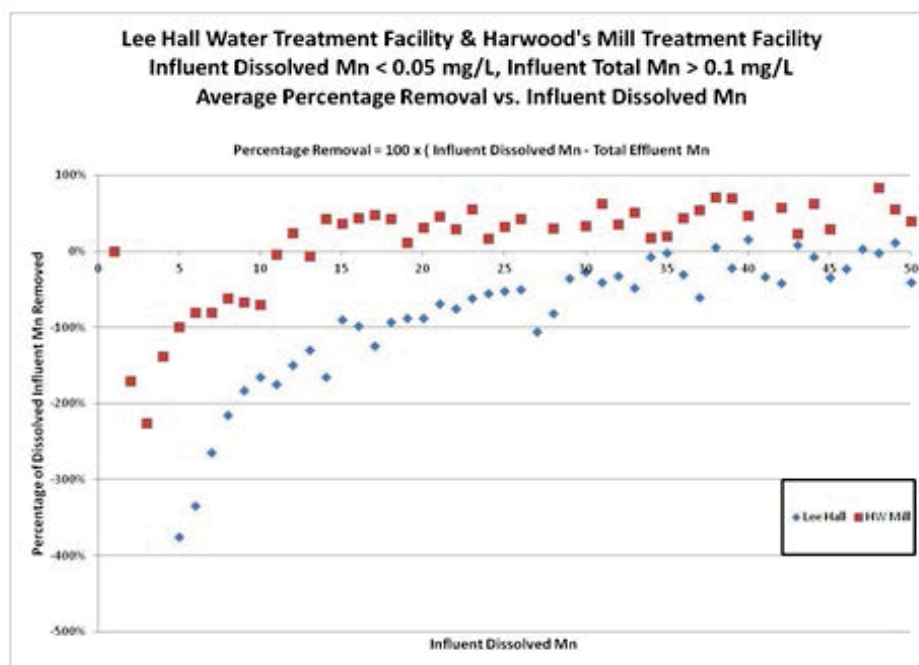
permanganate was being fed to the influent water; also, ozonation of both waters was practiced routinely during treatment.

The data presented in Figure 7.19 represent a few hundred observations of this raw water scenario within both water treatment facilities. These data have been consolidated to generate Figure 7.20, which presents the average observed Mn removal across both treatment facilities as a function of the raw water dissolved Mn concentration. A clear difference in Mn removal behavior was noted when comparing average Mn removal values observed at the Lee Hall facility versus the Harwood's Mill treatment facility. The results shown in Figure 7.19 (and consolidated in Figure 7.20) show clearly that the presence of substantial amounts of particulate Mn evidently generates the opportunity for reduction of some of this oxidized, particulate Mn at some point in the treatment process (e.g., possibly in any realm where anoxic conditions could exist and lead to Mn reduction and dissolution into solution). This clearly must happen at times within the Lee Hall treatment facility as this would be the only rational explanation for the observed behavior of the facility regarding an apparent lack of overall Mn removal (and possible release of dissolved Mn to the water during its passage through the treatment facility). The data in Figures 7.19 and 7.20 likewise show the benefit of having a  $\text{MnO}_x(\text{s})$ -coated filter media (coupled with free chlorine application) as part of the treatment train at the Harwood's Mill facility as this "net negative Mn removal" scenario basically was not observed. This again demonstrates the value of having  $\text{MnO}_x(\text{s})$ -coated filter media and filter-applied free chlorine to serve as a polishing step for dissolved Mn control near the end of the overall treatment train.



**Figure 7.19 Observed Mn removal behavior at both Newport News treatment facilities when significant particulate Mn was present in the raw water**





**Figure 7.20 Consolidation of Figure 7.19 observations on Mn removal to demonstrate difference in behavior for Mn control across the Lee Hall and Harwood's Mill Treatment Facilities**

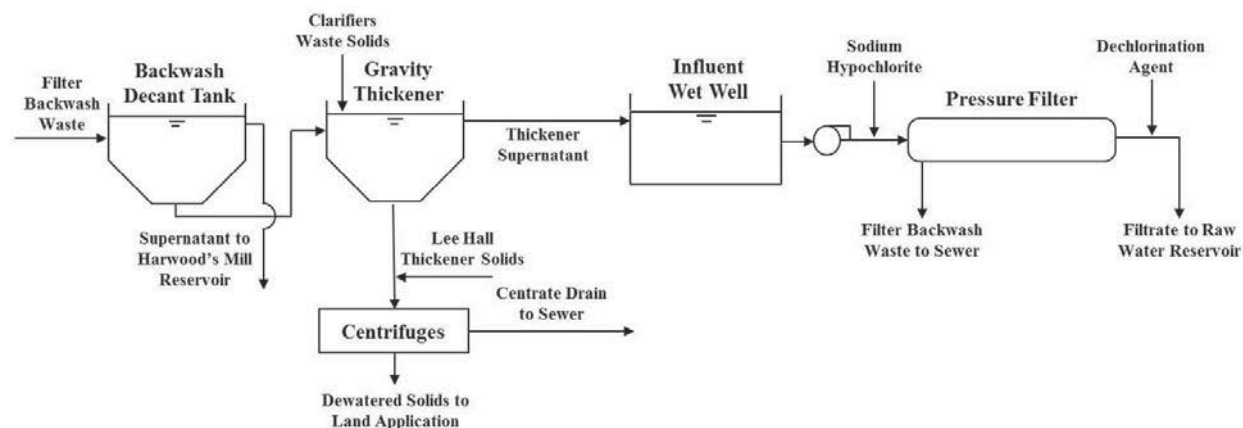
The following comments summarize the Mn removal effectiveness observed for both Newport News Waterworks treatment facilities. In general, both treatment facilities (Lee Hall and Harwood's Mill) are very effective in their efforts to produce finished water Mn concentrations at or below the secondary MCL of 0.05 mg/L. Further conclusions from the data analyzed from both treatment facilities are:

1. Permanganate can be effectively used as a pre-oxidation step (prior to coagulant addition) for addressing elevated dissolved Mn concentrations that appear periodically during the year. Both plants make effective use of this chemical in a pre-oxidation mode. Consideration of the use of sodium permanganate over the tradition potassium permanganate feed source can likewise be justified in certain treatment situations.
2. The presence of ozone during the treatment train does not add significant value in relation to dissolved Mn control; further, some evidence exists for the formation of colloidal  $\text{MnO}_x(\text{s})$  solids by ozone addition. Such solids may be difficult to capture in dual-media filters without some form of filter aid coagulant addition.
3. Overall Mn control was significantly aided at the Harwood's Mill treatment facility due to the presence of  $\text{MnO}_x(\text{s})$ -coated media in the dual-media filters coupled with free chlorine addition to the filter-applied water. This benefit was especially noticeable in the summer months when the average finished water Mn concentration at this facility was significantly below that observed at the companion Lee Hall facility.

### ***Manganese Control for Residuals Handling Systems***

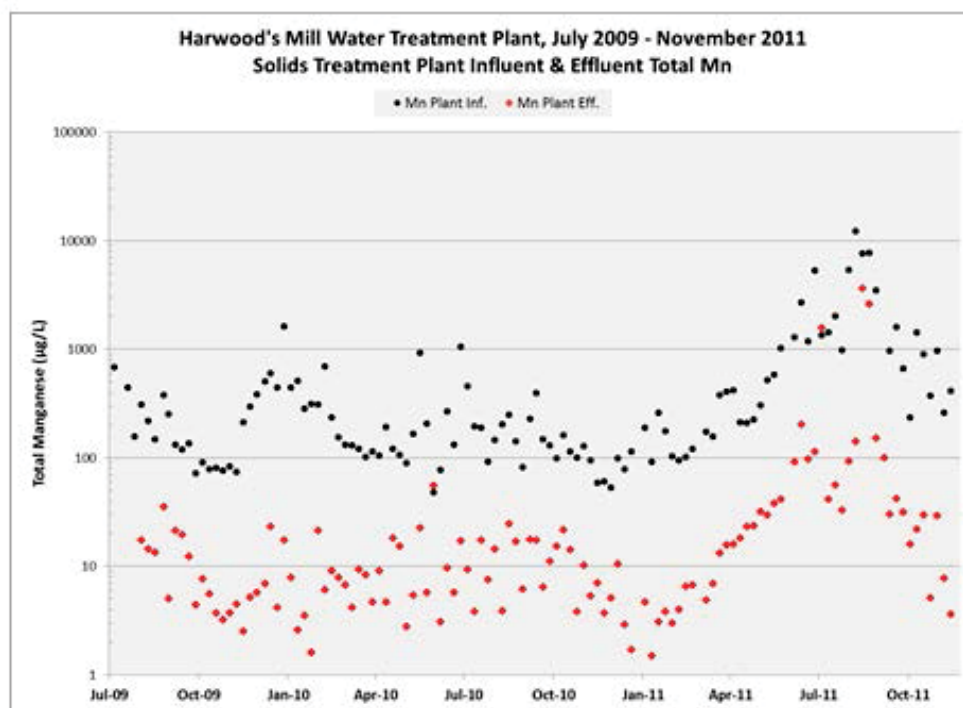
The waste residual solids produced from both the Lee Hall and Harwood's Mill treatment facilities are co-processed through a residuals handling system located onsite at the Harwood's Mill facility. A schematic of that residuals handling system is shown in [Figure 7.21](#). Waste residual solids at the Lee Hall facility are gravity thickened onsite and then pumped to the Harwood's Mill location. Two types of waste solids are generated at Harwood's Mill for residuals processing. Solids obtained during filter backwashing are gravity settled, with the supernatant from the backwash decant tank being discharged back to the terminal Harwood's Mill Reservoir and the accumulated solids pumped to a gravity thickener. Solids from the Superpulsator clarifiers are also directed to the gravity thickener and co-thickened with the solids from the backwash settling basin. The concentrated solids from the thickener are mixed with the thickened solids from the Lee Hall facility and further dewatered using high-speed centrifuges, generating dewatered cakes with 18-22 % dry solids that are subsequently applied to forested lands owned by the Waterworks for ultimate disposal. The centrate from this dewatering operation was found to contain extremely high Mn concentrations (often above 5000-10000 µg/L Mn), so the decision was made to discharge the centrate stream to a local sanitary sewer and not recycle this liquid back to the terminal reservoir.

Numerous research studies as well as testing in full-scale treatment facilities have shown that allowing MnO<sub>x</sub>-laden concentrated suspensions or thickened residuals waste streams to go anoxic can result in substantial releases of dissolved Mn into the liquid phase. This was likewise found to be true at the Harwood's Mill residuals handling system. Sampling of the supernatant discharged from the gravity thickener over several months showed that the dissolved Mn concentration present in the supernatant was highly variable; further, that dissolved Mn concentrations up to 10,000 µg/L could be obtained. Preliminary mass balance calculations showed that the release of this supernatant water back to the terminal Harwood's Mill Reservoir would significantly increase the total Mn loading to the reservoir, hence increasing the potential raw water Mn concentration that would require treatment. As a result Newport News Waterworks personnel undertook a pilot-scale feasibility study to demonstrate the effectiveness for using a MnO<sub>x</sub>(s) filter media for treating the gravity thickener supernatant flow prior to its release to the reservoir. Following a successful pilot-scale study the Waterworks constructed a full-scale treatment system for the gravity thickener supernatant that involves free chlorine addition to the water followed by passage of the water through MnO<sub>x</sub>(s)-coated media in a pressure filter. The free chlorine dosage to the water is maintained at a level that yields a 1 mg/L free chlorine concentration in the filtrate from the pressure filter. The water is then dechlorinated after filtration and prior to release to the terminal Harwood's Mill Reservoir. The backwash water from the pressure filter is sent to a local sanitary sewer.



**Figure 7.21 Schematic of the residuals processing system employed by the Newport News Waterworks at the Harwood's Mill Treatment Facility**

Results from a thirty-month period of operation of this Mn treatment system are shown in Figure 7.22. The data presented again demonstrate the highly variable Mn concentration present in the gravity thickener supernatant. While some of the Mn present is particulate the vast majority of it was found to be in the form of dissolved Mn. The data presented in Figure 7.22 clearly demonstrate the effective Mn removal being achieved across the  $\text{MnO}_x(\text{s})$ -coated media system; analysis of the data over this time period yielded an average Mn removal for the treatment system in excess of 90%. Further, most of the Mn concentrations leaving the pressure filter were at or below the secondary MCL for Mn of 0.05 mg/L. As such, the implementation of this  $\text{MnO}_x(\text{s})$ -coated media treatment system coupled with the decision to put the liquid centrate into a nearby sanitary sewer resulted in a major reduction in the amount of Mn being recycled from the onsite residuals handling system into the terminal Harwood's Mill Reservoir. Likewise, analysis of the Mn concentrations present in the terminal Harwood's Mill Reservoir water indicate a positive benefit (e.g., reduced Mn concentrations in the raw water to the Harwood's Mill facility) from implementing these Mn control measures within the residuals handling system.



**Figure 7.22 Performance of the  $\text{MnO}_x(\text{s})$ -coated pressure filter media for removing Mn from the gravity thickener supernatant stream**

## AQUARION WATER COMPANY OF CONNECTICUT

**Problem:** 1) Control of annual seasonal increase in raw water Mn for surface water reservoirs; 2) control of Mn, Fe, DBPs with direct filtration for a groundwater source.

**Solution:** 1) Routine monitoring and use of pre-filter chlorination (continuously or seasonally) and Mn-oxide coated traditional filter media; 2) convert to a two-stage pressurized process of dual-media filtration for particle removal (Fe and some TOC) and a post-filter contactor for Mn removal by sorption and catalytic oxidation.

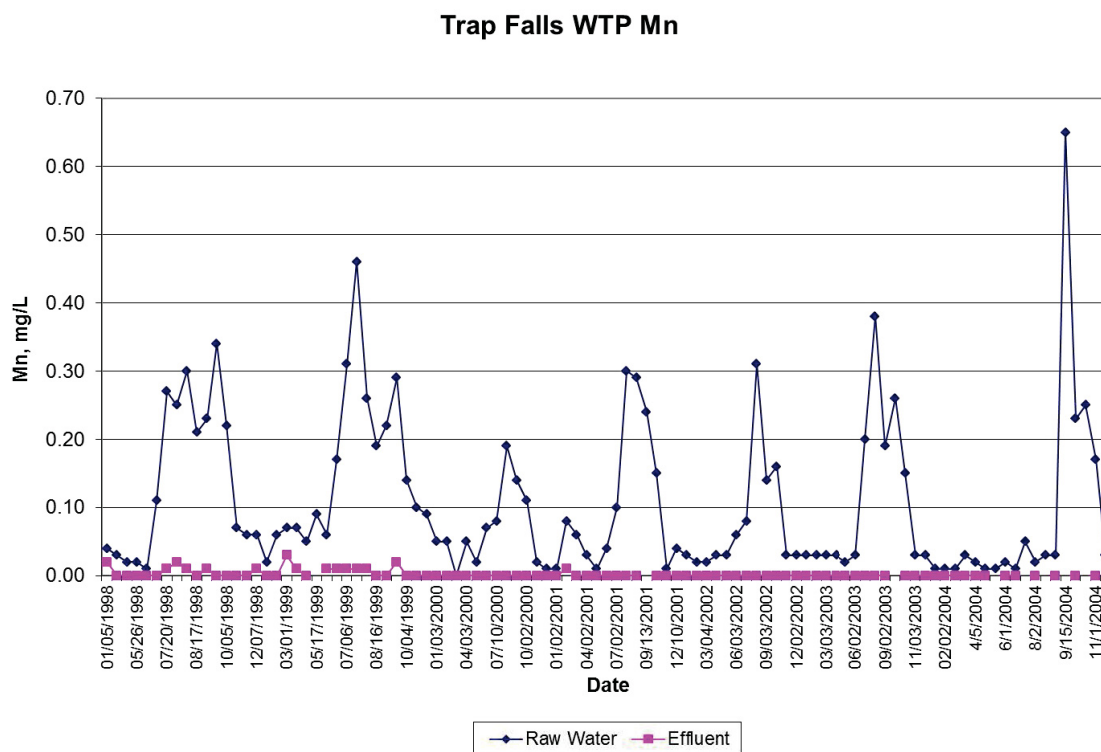
### *Background*

Aquarion Water Company of Connecticut (AWC), a private water company that supplies water to over 600,000 people in the state of CT, has numerous treatment facilities including larger and smaller plants with surface water sources as well as smaller capacity facilities with groundwater sources. This case study summarizes Mn control strategies used for the surface water plants and an innovative approach for a challenging groundwater source.

### *Results*

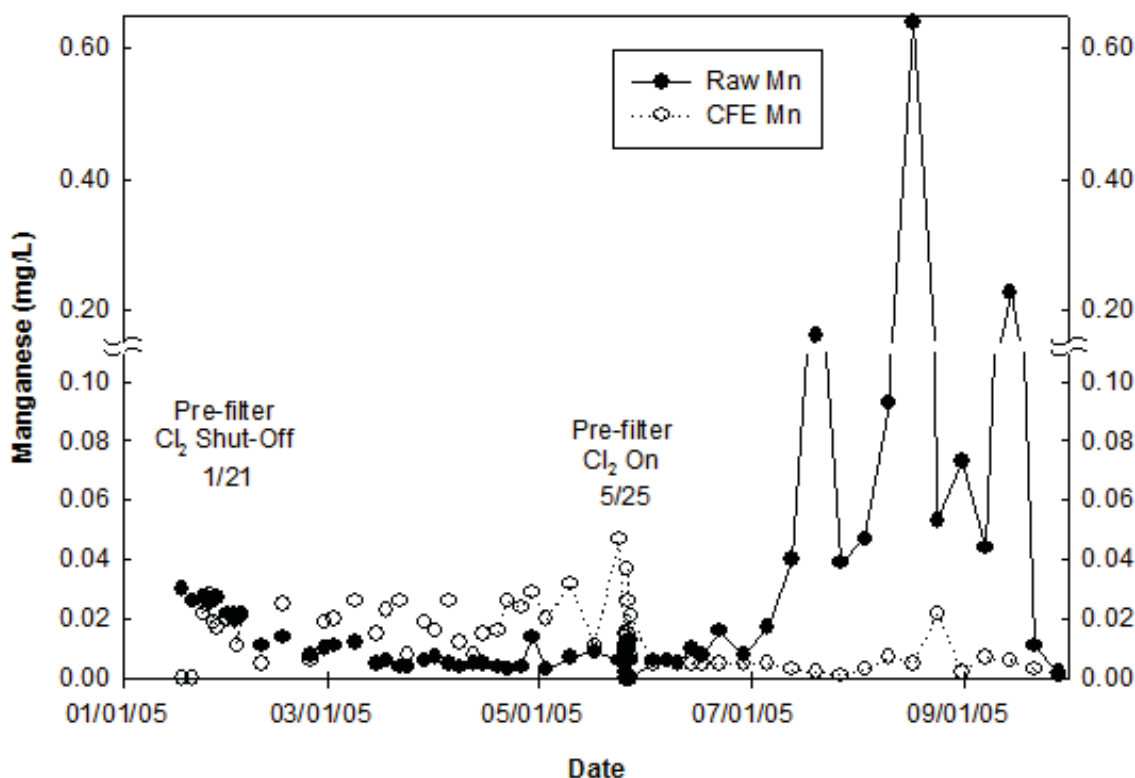
Surface Waters: AWC has four larger (~ 20 to 50 MGD capacity) surface water plants in southwestern CT, each supplied with soft, low alkalinity, pH 6.5 to 7.5, low turbidity and moderate TOC water from one or more typical New England reservoirs. These reservoirs undergo typical seasonal patterns of thermal stratification and mixing. Raw water Mn levels are low (e.g., < 0.03 mg/L) much of the year but typically display annual summer/fall increases to much higher levels (e.g., 0.1 to 0.4 mg/L, approximately). Several of the plants were designed and constructed with reactors for short-duration pre-oxidation (e.g.,  $\text{KMnO}_4$  addition, several minutes of reaction time) prior to coagulation, flocculation, clarification (either plate sedimentation or dissolved air flotation) and dual media (anthracite over silica sand) filtration. AWC optimizes coagulation to maximize TOC removal, most of which occurs through the clarification process. Despite the presence of a process tank for pre-oxidation in some plants, AWC has typically chosen to consistently achieve very low (e.g., < 0.02 mg/L) filter effluent Mn levels by the use of pre-filter chlorination and Mn-oxide coatings on the traditional anthracite and sand filter media. As published previously (Tobiason et al., 2008; Islam et al., 2010), levels of Mn on the anthracite were in the range of 10 to 40 mg Mn per gm of media. Typical data for raw and filter effluent Mn levels for one of the plants (Trap Falls) for a six year period are shown in [Figure 7.23](#) (similar to data from Tobiason et al., 2008, Appendix B); despite seasonal spikes in raw water Mn, filter effluent levels are always low. AWC prefers to remove Mn via pre-filter chlorination and oxide coated media as the approach is robust and straightforward to control by maintenance of a desired minimum filter effluent chlorine residual, in contrast to the need to apply the correct  $\text{KMnO}_4$  dose as raw water Mn levels change. In addition, AWC utilizes free chlorine for primary and secondary disinfection. AWC has typically followed the approach described in Knocke et al. (1990) to initiate the Mn-oxide media coating by *in-situ* soaking of new filter media in a  $\text{KMnO}_4$  solution.





**Figure 7.23 Raw and *filter* effluent Mn levels, AWC Trap Falls plant, 1998-2004**

The clarification process removes the majority of the TOC that is removed by the AWC plants, with a minor amount (perhaps < 0.2 to 0.3 mg/L of TOC) removed by granular media filtration. However, AWC and researchers at the University of Massachusetts decided to assess the impact of pre-filter chlorination, versus only post-filter chlorination, on the formation of DBPs. Data (e.g., Corbin et al. 2003; Tobiason et al., 2008) showed that elimination of pre-filter chlorination resulted in DBP (TTHM and HAA5) level decreases of 5 to 50%. As such, AWC has also investigated and selectively implemented the use of discontinuous pre-filter chlorination, e.g., not applying pre-filter chlorine when raw water Mn levels are very low. Results for one plant (Stamford), in its 2005 configuration of sand only filter media following conventional sedimentation, showed that effective Mn uptake capacity was quickly restored by re-starting pre-filter chlorination after a four month period of no pre-filter chlorination (Figure 7.24, from Islam et al., 2010) and that there was no measurable loss of Mn-oxide coating on the media. The results in Figure 7.24 do show that filter effluent Mn levels actually exceeded very low raw water Mn levels for a period of time, suggesting that a very low level of Mn release from the media may have occurred.



**Figure 7.24 Raw and combined filter effluent Mn levels, AWC Stamford plant, 2005.**

The AWC Stamford plant was replaced in 2007 by a plant employing coagulation, flocculation, dissolved air flotation and dual media filtration and the practice of pre-filter chlorination and oxide-coated media for control of seasonal spikes in raw water Mn was continued. While discontinuation of pre-filter chlorination may be desirable for minimizing DBPs, careful attention to filter effluent Mn levels is needed as Mn release from media coatings can develop rapidly, probably via biological reduction and dissolution. Data for raw and filter effluent Mn levels for the Stamford plant for 2012 shown in [Figure 7.25](#) illustrate this phenomenon. From January through mid-April, with pre-filter chlorination in use, raw water Mn levels of ~ 0.02 mg/L were decreased to < 0.01 mg/L. However, discontinuation of pre-filter chlorination in mid-April was followed by an increase in filter effluent Mn to levels far exceeding the raw water level such that pre-filter chlorination was re-instated in mid-May, resulting in a rapid (two days) return to filter effluent levels of ~ 0.01 mg/L, again below the then low raw water levels and continued excellent Mn removal as raw water Mn levels increased to as high as 0.15 mg/L in August.

Data for raw and filter effluent Mn for February 2011 through August 2012 for another AWC plant (Easton) are shown in [Figure 7.26](#). In contrast to the Stamford data, the results for Easton show three month duration periods in both 2011 and 2012 where pre-filter chlorination was discontinued without causing the filter effluent Mn level to ever exceed the low raw water levels, indicating no release of Mn occurred. The data also show another example of control of elevated raw water Mn levels by application of pre-filter chlorination from June 2011 through mid-February 2012.

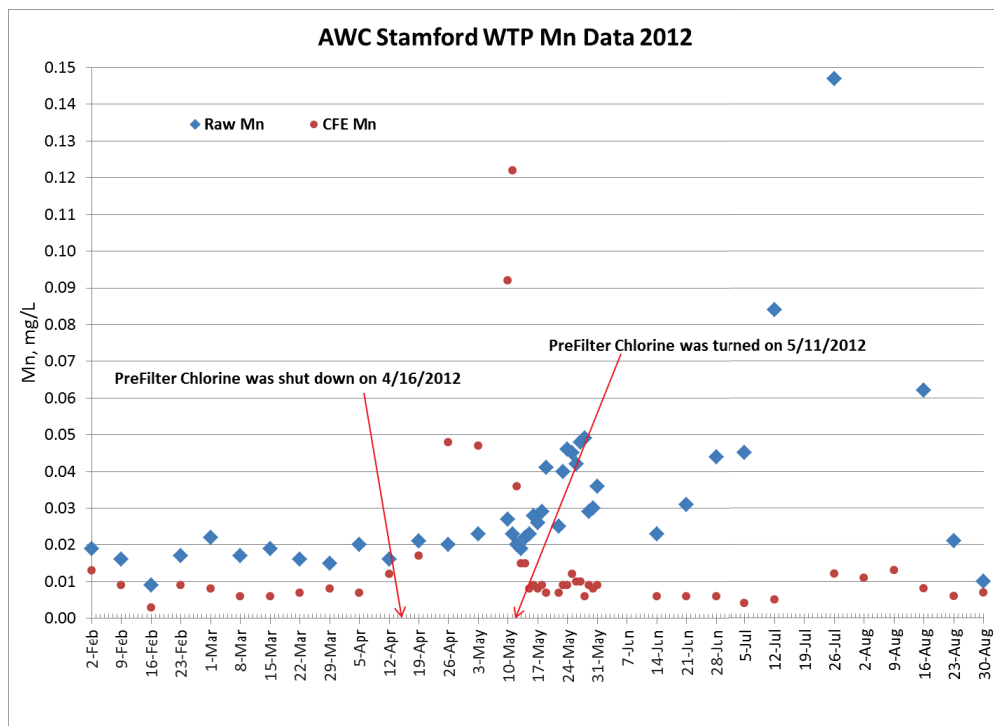


Figure 7.25 Raw and combined filter effluent (CFE) Mn levels, AWC Stamford plant, 2012

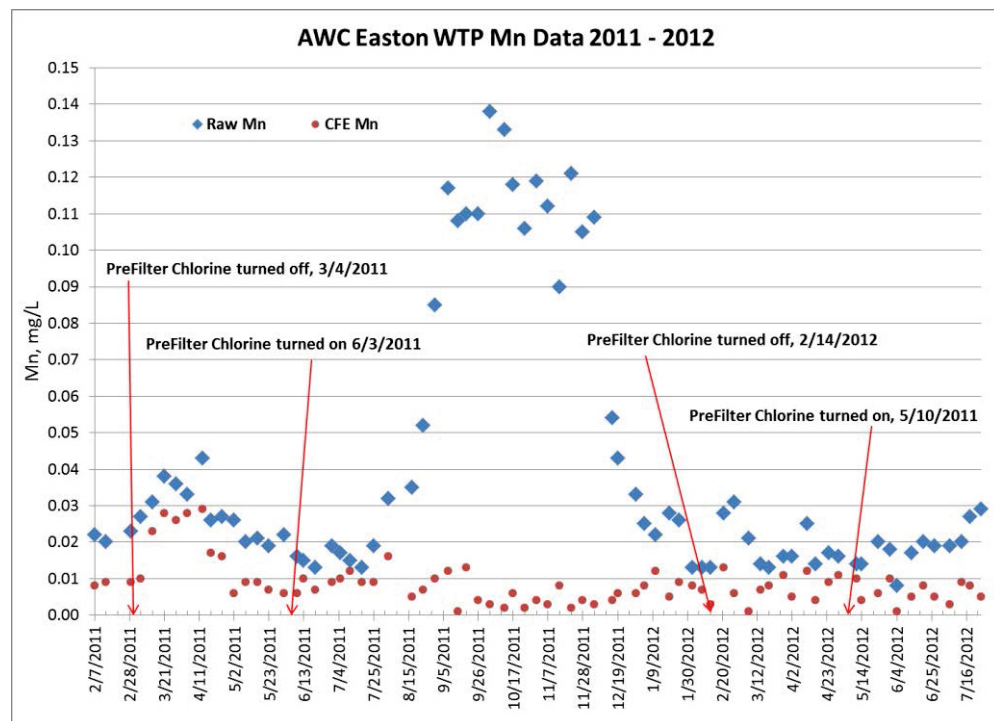
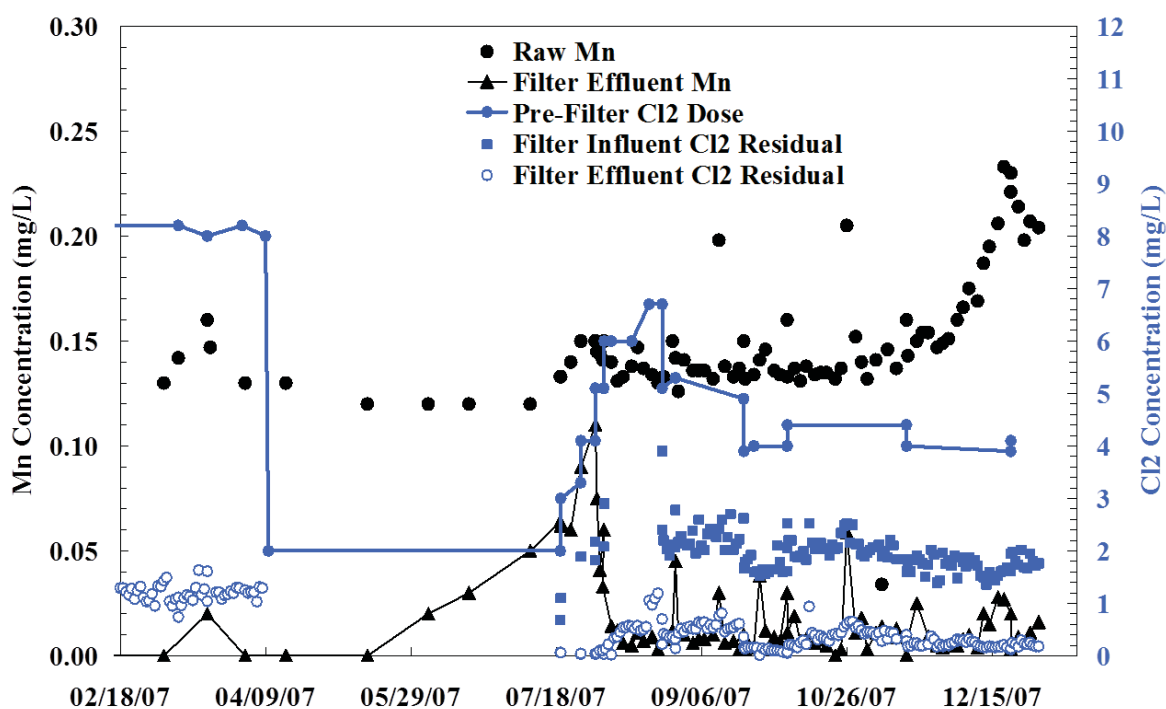


Figure 7.26 Raw and combined filter effluent (CFE) Mn levels, AWC Easton plant, 2011-2012

As the data for Stamford and Easton illustrate, the impact of discontinuation of pre-filter chlorination on Mn release from filter media is very variable, ranging from no impact to a very slow increase at a very low level, to a rapid increase to unacceptably high levels. Regular monitoring of filter effluent Mn levels is needed to properly manage the intermittent application of pre-filter chlorine ahead of Mn-oxide coated dual media filters.

**Ground Water Source:** The AWC Lantern Hill ground water supply in Stonington, CT has historically been treated by pre-oxidation ( $\text{KMnO}_4$  and chlorine, with pH control and polymer dosing) and dual-media (anthracite over greensand) pressure direct filtration for removal of elevated raw water levels of iron (1.5 to 2.5 mg/L), manganese (0.15 to 0.25 mg/L) and TOC (2.5 to 4.5 mg/L). Until 2007 the treatment plant relied on only pre-filter addition of chlorine to achieve the  $\sim 1$  mg/L desired chlorine residual entering the distribution system. Although effective Fe and Mn removal were achieved, the required high (5 to 8 mg/L) pre-filter chlorine dose resulted in very high filter effluent DBP levels. In the spring of 2007 post-filter dosing of chlorine was added and the pre-filter chlorine dose was decreased to 2 mg/L. Unfortunately, after 45 to 60 days of operation, filter effluent dissolved Mn rapidly increased, indicating release of Mn from the filter, most likely due to microbiological reduction. Pre-filter chlorine dosing was subsequently increased to 4 to 6 mg/L to yield a filter effluent chlorine residual of  $\sim 0.2$  mg/L, resulting in a return to very low ( $< 0.02$  mg/L) filter effluent Mn levels, but also with very high DBP formation. Manganese and chlorine data for the Lantern Hill plant during this time period are summarized in Figure 7.27.

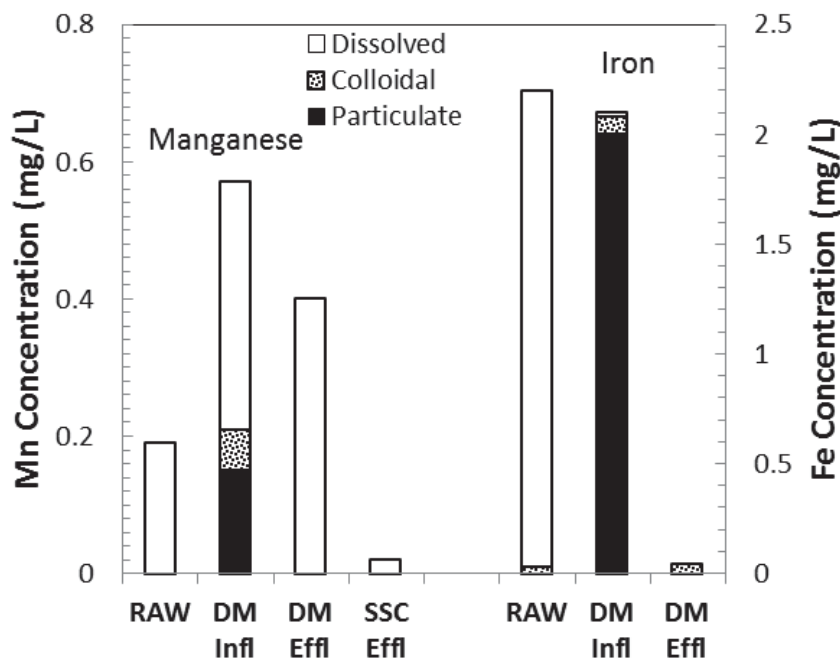


**Figure 7.27 Manganese and chlorine data, Lantern Hill WTP, AWC of CT**

AWC and researchers at the University of Massachusetts undertook a series of pilot-scale studies to assess feasible strategies that maintained the well-pump only based pressurized treatment system while meeting water quality goals. The final result of the pilot-scale research

was the design and construction of a new full-scale two-stage process expected to be operating by mid-2013. In the upgraded plant the three parallel existing dual-media greensand filters are converted to conventional anthracite over silica sand dual-media filters with a design hydraulic loading rate (HLR) of 3 gpm/ft<sup>2</sup> (same as the current filters). A new set of three parallel second stage 40 inch deep coarse media (~ 2 mm) Mn removal contactors, operated at a design HLR of 10 gpm/ft<sup>2</sup>, are added after the dual-media filters; free-chlorine is dosed ahead of the contactors to achieve a contactor effluent chlorine residual of ~ 1 mg/L. Pre-filtration chemical addition includes NaOH for pH control (7.0 to 7.2), either KMnO<sub>4</sub> or NaOCl for iron oxidation and a cationic polymer for improved particle (and TOC) removal. The pilot research has shown that a low (~ 2 to 3 mg/L) dose of pre-filter chlorine achieves rapid Fe oxidation with minimal DBP formation; use of only one oxidant may be desirable from an operational perspective.

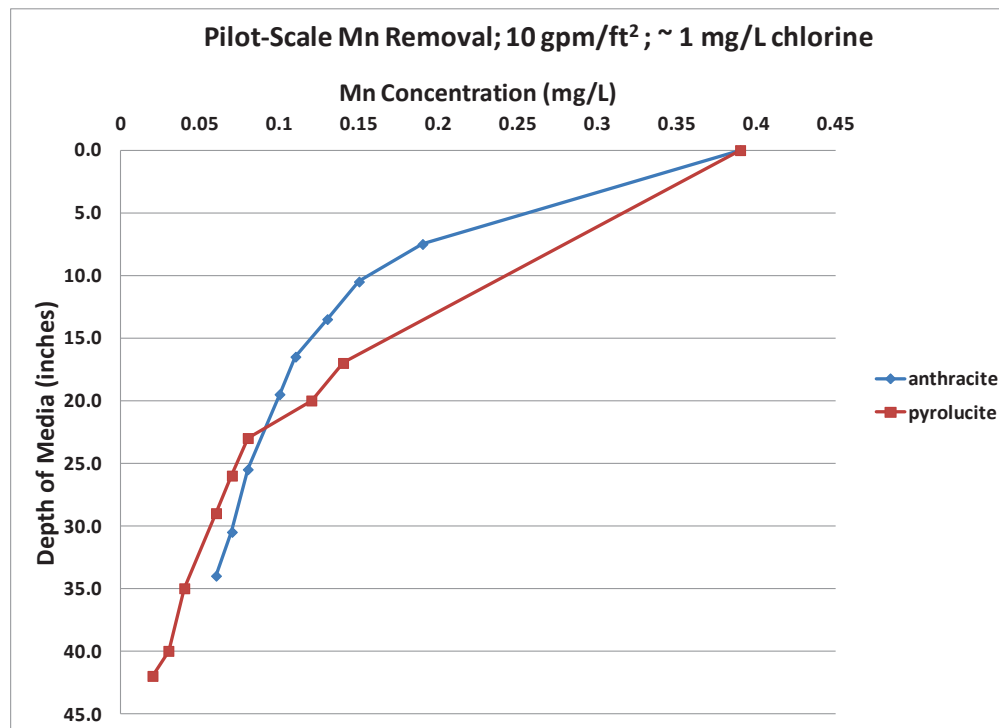
The low level pre-oxidant dosing results in complete Fe oxidation, allowing for removal by particle filtration (including ~ 1 mg/L of the raw water TOC), yet little, if any, Mn oxidation. Data for Mn and Fe fractionation across the pilot treatment processes in August 2011 when pre-oxidation with KMnO<sub>4</sub> was utilized are shown in Figure 7.28. Raw water Fe, all in the reduced, dissolved form, is oxidized to particulate form and completely removed by the dual media (DM) filter. Manganese, also dissolved in the raw water, shows an increase in total amount due to permanganate addition and a significant fraction remains dissolved in the DM filter influent. There is no removal of dissolved Mn by the DM filter, but all the DM filter effluent Mn (which is all dissolved) is subsequently removed by sorption and catalytic oxidation (by the free chlorine) on the surface of the coarse media Mn contactor.



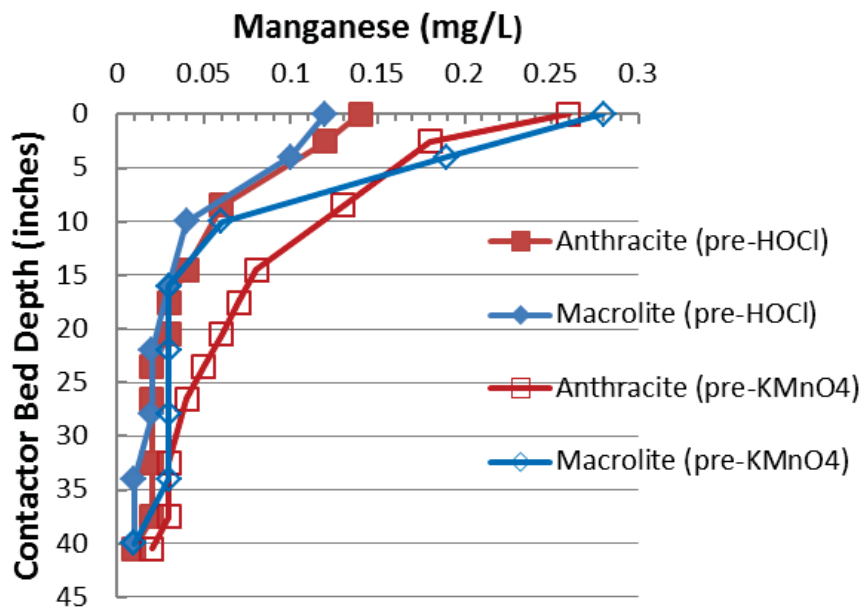
**Figure 7.28** Manganese and iron fractionation across the Lantern Hill two-stage pilot treatment process, August 2011. DM: dual-media filter (3 gpm/ft<sup>2</sup> HLR); SSC: second-stage contactor (10 gpm/ft<sup>2</sup> HLR). Pre-oxidation using 1.4 mg/L KMnO<sub>4</sub>.



Extensive laboratory and pilot-scale studies of various types of media for the Mn contactors were undertaken. All media performed well with *in-situ* coated anthracite and a commercially coated ceramic media, both of low density, showing the best results. Figure 7.29 in this report shows profiles of Mn removal across contactors for two of the media types (pyrolucite and anthracite) while Figure 7.30 shows additional pilot study results for Mn removal across the contactors for parallel anthracite and Macrolite media types. The most important result of the pilot studies was the 55 to 75% decrease in plant effluent and 24 hr simulated distribution system levels of TTHM and HAA5 DBPs that resulted from the two-stage process as compared to the existing full-scale single-stage direct filtration process. This dramatic decrease resulted from delaying the addition of most chlorine until after some TOC removal occurred and from not applying free chlorine across the dual-media particle removal filtration stage (there is no chlorine residual entering the dual-media filter when the low (2 to 3 mg/L) pre-chlorine dosing is used for iron oxidation).



**Figure 7.29 Comparison of Mn removal by media depth of anthracite and pyrolucite contactors**



**Figure 7.30 AWC Lantern Hill pilot-scale manganese versus second stage contactor depth profiles for Mn-oxide coated anthracite and commercial ceramic (Macrolite) media types, August 2012. 10 gpm/ft<sup>2</sup> hydraulic loading rate. pH~7.3, ~1.3 mg/L residual chlorine in contactor effluent.**

## METROPOLITAN WATER DISTRICT OF SOUTHERN CALIFORNIA

**Problem:** Customer complaints of colored water after installing pre-ozonation followed by biologically active filtration.

**Solution:** Filter media replacement.

### *Background*

At the Mills Filtration Plant in Riverside, CA, Metropolitan Water District of Southern California (MWDSC) elected to make changes in the treatment process to meet the alternative treatment technique requirements of the Stage 1 Disinfectant/Disinfection Byproduct Rule (Stage 1 DBPR) and to reduce the overall production of disinfection byproducts. The Stage 1 DBPR allows treatment plants with less than 4.0 mg/L of total organic carbon (TOC) and 60 mg/L of alkalinity (on a running annual average basis) to use alternative treatment techniques instead of operating in the enhanced coagulation mode. By installing pre-ozonation followed by biologically active filtration, the Mills plant meets the alternative treatment technique requirements and obtains other benefits such as taste and odor control at a reasonable cost.

In the process of switching the Mills plant from pre-chlorination to pre-ozonation followed by biologically active filtration, reservoir effluent turbidities became elevated and numerous customer complaints of colored water were received. The problem at the plant was traced to Mn leaching from the plant filter media. Particulate Mn was being formed in the combined filter effluent after the water was pH adjusted upward and chlorinated. The problem was surprising because the plant influent Mn levels are typically less than 0.01 mg/L, well below the secondary MCL of 0.05 mg/L.

The short term response to releasing Mn was to resume filter influent chlorination at a chlorine dose between 1.0 and 1.5 mg/L  $\text{Cl}_2$  to halt any further release of Mn from the plant while remediation options and operational strategies were evaluated.

### *Evaluation*

Three sources of Mn were identified within the Mills Filtration Plant: influent source water, coagulant solution and washwater return. The influent source water had 9-12  $\mu\text{g/L}$  total Mn entering the plant. Between 16 and 64  $\mu\text{g/L}$  total Mn was found leaving the sedimentation basins, suggesting potential Mn contamination of the  $\text{FeCl}_3$  coagulant. Initially, the Mills plant was receiving bulk  $\text{FeCl}_3$  that contained upwards of 1,000 mg/L Mn. This resulted in up to 28  $\mu\text{g/L}$  of dissolved Mn being added at the rapid mix when 20 mg/L of  $\text{FeCl}_3$  was added. Later  $\text{FeCl}_3$  supplies contained 500 mg/L Mn and 250 mg/L Mn, which lessened the Mn load to the flocculation/sedimentation basins. The washwater return stream contained 100 – 7,700  $\mu\text{g/L}$  Mn as it was decanted to the head of the plant prior to ozone addition, a source which was a side effect of the Mn in the  $\text{FeCl}_3$  supply.

A survey of Mn deposition in the filter media of MWDSC's five drinking water treatment plants showed that all the filters contained Mn deposits. At the time that the new ozone systems were brought on line, only the Mills plant had tried to operate biologically without the chlorine

feed to the filters, so it was the only plant experiencing the colored water complaints. Concentrations in the media ranged from 390-1,500 mg Mn/kg anthracite, 2,900-3,500 mg Mn/kg sand and 4,100-8,700 mg Mn/kg hematite. The plant had been utilizing  $\text{FeCl}_3$  as a coagulant for 11 years at a ferric dose of 5-30 mg/L.

Both pilot and full-scale testing were utilized to evaluate remediation options and operational strategies that included the following:

- Controlled release of Mn using ferric chloride ( $\text{FeCl}_3$ ) or by switching to aluminum sulfate (alum) coagulation.
- Controlling Mn recirculation within the plant.
- Media cleaning using proprietary inorganic acid and reducing agents.
- Media replacement.
- Altering chemical addition points for pH control at filter inlet.
- Sequestration of dissolved Mn using polyphosphate.

Controlled Release of Mn. Controlling the release of Mn from filters was tested by limiting the number of non-chlorinated filters in service at one time. The test was performed using both  $\text{FeCl}_3$  and alum coagulation. For the  $\text{FeCl}_3$  test, one filter was dechlorinated with sodium thiosulfate to facilitate Mn release. The alum test was completed by discontinuing filter inlet chlorination. Results of the testing showed that the filter effluent Mn was primarily dissolved and the  $\text{FeCl}_3$  coagulation without chlorine released Mn at approximately four times the level compared to alum. The release from the filters lasted 3.5 weeks. The addition of thiosulfate to the filter resulted in a substantial increase in headloss across the filter and filter backwashing was increased by a factor of three.

At full-scale, the plant started operating a group of 5 non-chlorinated filters and blended with water from 16 chlorinated filters. The 5 filters were monitored closely for Mn release, which showed variations in Mn desorption behavior between filters operated under the same treatment conditions. As fresh non-chlorinated filters were brought on line, plant effluent turbidity and particle counts rose. The number of new non-chlorinated filters added was then limited to two at a time to control finished water quality.

Controlling Mn Recirculation within the Plant. During the testing with alum coagulation, the plant found that a large portion of the Mn was being returned to the head of the plant from the water return stream. Mn levels in the return stream peaked at 250  $\mu\text{g/L}$  Mn. The Mn in the sludge lagoons under this operating condition was assumed to be scoured from the filter media. Particulate Mn was still being removed from filter media after two months. Testing of the sludge lagoons showed Mn levels ranging from 40 to 7,650  $\mu\text{g/L}$  Mn, of which greater than 90 percent was dissolved. To manage this source of Mn, individual sludge basins were taken out of service and the water was not returned to the head of the plant when the Mn level exceeded 500 mg/L Mn.

pH Control at Filter Inlet. At pilot scale, MWDSC was able to evaluate the effect of pH at the filter inlet on Mn release from the filters. Mn release was shown to be a function of pH, where with declining pH the concentration of Mn released increased. At ambient pH (pH 8.0) using either  $\text{FeCl}_3$  or alum, Mn release was not favored. The data suggest that by operating the filters under slightly alkaline conditions, Mn desorption may be controlled for the short term.

Media Cleaning. Removal of Mn from filter media relies on dissolving the  $MnO_x(s)$  coating to mobilize the Mn and then flushing the dissolved Mn from the system. MWDSC used a commercial product from Floran Technologies, Inc., that is a two-step process involving the addition of a strong reducing acid followed by a peroxide “catalyst” to the bulk media. The cleaning reagents are added on the top of the media without mixing, so the success of Mn removal was measured on separate layers of filter media at pilot scale. The upper layer of anthracite was cleaned relatively well (97 percent removal), while removal from the mid-layer of sand was only 47 percent and from the bottom layer of hematite was approximately 4 percent. Increasing the acid portion of the cleaner by 2, 4 and 8 times did improve removal, but not in a linear mode.

The pilot filter that was cleaned was returned to service after cleaning without any major problems. No Mn was released from the media post-cleaning treatment and filter turbidity returned to normal within 2 hours of placing the filter back into service. MWDSC chose not to pursue this option after considering the cost of disposal for greater than 50,000 gal/filter of < pH 2 Mn-laden waste. A cost proposal was received from the chemical vendor in association with a waste disposal company for \$32/ft<sup>2</sup> to clean filter media. The cost included neutralization and clarification of the liquid waste stream and disposal of the waste solids.

Sequestration with Polyphosphates. A dose of 2.0 mg/L polyphosphate successfully sequestered 105 µg/L of Mn for 10 days of holding time. The sample was chlorinated for 5 minutes with 3.0 mg/L of chlorine, pH adjusted to 8.3 and held for 8.9 hours contact time with chloramines. Despite these results there remains the prospect that sequestered Mn could be destabilized, releasing Mn into the distribution system. This Mn in turn could (and probably had already) accumulated in the distribution system. MWDSC was concerned that there was the possibility of resolubilization of accumulated Mn and iron from unlined cast iron and steel pipes and possible resuspension of HPC bacteria. Although these problems may be short-term, the use of polyphosphates may trade one water quality problem for another, so the option was not pursued further.

Media Replacement. Due to the timeframe in which the filtration plants needed to be on-line with O<sub>3</sub>/biofiltration, the utility decided to replace the media for two of the treatment plants, including the Mills plant. Complete filter media replacement was recommended for the Mills plant.

### ***Conclusions/Recommendation***

Test results suggest that the majority of Mn in the filter media accumulated over multiple years of using Mn-containing FeCl<sub>3</sub> for coagulation. Major findings related to Mn desorption from filter media include:

- Coagulant selection plays an important role in Mn release. During full-scale testing, FeCl<sub>3</sub> coagulation without chlorine released dissolved Mn at nearly four times the level compared to alum.
- Mn-release events typically last two to three weeks for individual filters.



- Chemical cleaning of the filter media was observed to clean upper layers of media (anthracite) more efficiently than lower layers (sand or hematite) in the filter.
- Polyphosphates, applied downstream of a biofilter, may successfully sequester up to 105 µg/L dissolved Mn with 10 days of detention time, but potential adverse effects are unknown.
- Media replacement was recommended as the optimum solution.

**SIOUX FALLS, SD****Problem:** Variable high levels of manganese in raw water supply.**Solution:** Utilize softening process to remove both hardness and manganese.***Background***

The City of Sioux Falls, SD, has three sources of raw water to feed their water purification plant, including the Big Sioux River, the Big Sioux Aquifer and the Middle Skunk Creek Aquifer. The predominant sources of supply are the 55 ground water wells which provided 91.7 percent of the total water produced in 2011. The remaining 8.3 percent of water produced in 2011 was surface water from the Big Sioux River. Average daily production of treated water is 18.5 MGD. Raw and finished water quality parameters are shown in [Table 7.2](#). Manganese levels in the raw water can be considerable, peaking at 2.48 mg/L in 2011.

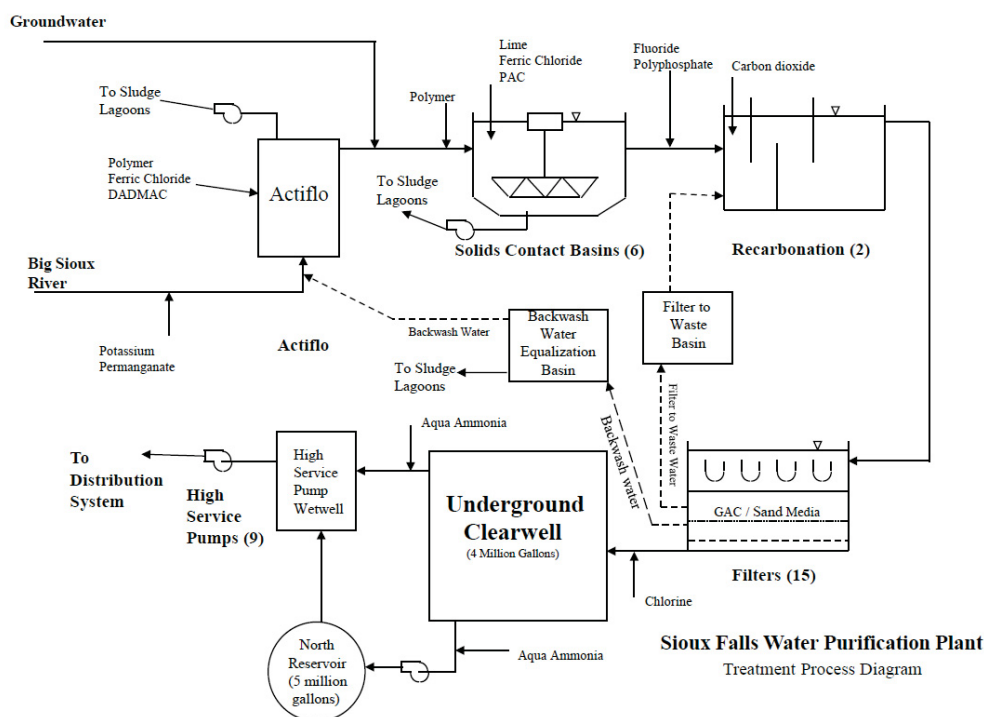
**Table 7.2**  
**Raw and finished water quality in 2011 for Sioux Falls**

Parameter	Raw Water Quality 2011			Finished Water Quality 2011		
	Average	Minimum	Maximum	Average	Minimum	Maximum
pH	7.38	7.00	7.86	8.33	7.66	8.90
Turbidity, NTU	11.70	0.60	100.00	0.06	0.03	0.11
Temperature, °C	11.6	4.0	20.8	11.4	7.8	17.8
Total Hardness (as CaCO <sub>3</sub> )	520	212	600	267	219	338
Calcium Hardness (as CaCO <sub>3</sub> )	321	238	480	116	86	147
Magnesium Hardness (as CaCO <sub>3</sub> )	199	109	314	151	101	218
Total Alkalinity (as CaCO <sub>3</sub> )	307	219	410	52	34	92
Total Dissolved Solids, mg/L	381	259	469	381	259	469
Iron, mg/L	1.41	0.01	10.78	0.01	BDL	.010
Manganese, mg/L	1.34	0.01	2.48	BDL	BDL	0.04
Total Organic Carbon, mg/L	3.6	2.00	4.98	2.75	1.88	3.37
Free Chlorine, mg/L				2.22	1.80	2.90
Total Chlorine, mg/L				2.47	2.00	2.80

BDL = below detection limit

When Sioux Falls is utilizing both surface and ground water, the surface water is pretreated before being blended with ground water and softened. A schematic diagram of the Sioux Falls Water Treatment Plant is shown in [Figure 7.31](#).

Sioux Falls depends on the softening process to remove manganese in the treatment plant. The plant operates at a softening pH of 9.9 to 10 to remove excess calcium by precipitating calcium carbonate. Ferric chloride and cationic polymer are used for coagulation in the Actiflo pretreatment process for surface water and intermittently in the softening process. Backwash waste water is reclaimed by recirculating the decant from the backwash basin to the Actiflo basin. Mn removal by the softening process remains consistent even though the influent Mn concentration in the surface water supply is variable and there are changing blends of surface water, ground water and backwash recycle water. Consistent Mn removal is accomplished by the softening process which takes advantage of Mn's low solubility at high pH conditions (See [Figure 2.1](#)). At high pH Mn forms insoluble oxides, hydroxides and/or carbonates that precipitate out of solution and are incorporated into the calcium solids formed by the softening process.



**Figure 7.31 Treatment process schematic for the Sioux Falls Water Purification Plant**

### *Practical Application*

As the water quality data demonstrate, finished water Mn at Sioux Falls is typically below the detection limit. This demonstrates the robust performance of softening for Mn treatment.

## FORT COLLINS, CO

**Problem:** Reservoir stratification elevating summer Mn to levels that were difficult to treat utilizing the existing conventional treatment plant.

**Solution:** Evaluate oxidants and oxidant doses at bench scale to determine preferred oxidant to form Mn oxide in the contact time available in the plant.

### *Background*

The City of Fort Collins, CO, Water Treatment Facility (FCWTF) is a conventional water treatment plant supplied by two surface water sources. One source is an intake on the Cache la Poudre River and the other intake is from Horsetooth Reservoir. A schematic diagram of the plant treatment processes is shown in [Figure 7.32](#). The plant processes include coagulation with alum added in the rapid mix basin, flocculation/sedimentation using inclined plants (detention time approximately 60 minutes), rapid-rate filtration using dual-media sand/anthracite filters and disinfection with chlorine. The available detention time between the raw water intake and the addition of alum in the rapid mix basin ranges from 120 to 300 seconds, depending on plant flow rate. During seasons when Mn is typically elevated, detention time is approximately 180-300 seconds. The available contact time is of importance to the plant in removing manganese because while using a temporary  $\text{KMnO}_4$  feed system, Fort Collins found that the oxidation of low level  $\text{Mn}^{2+}$  was effectively stopped by the depression of pH from 7.0 (raw water) to 6.3-6.4 in the rapid mix due to the addition of alum.

During the 1990's, the FCWTF experienced  $\text{Mn}^{2+}$  levels up to 0.450 mg/L in Horsetooth Reservoir, although the typical  $\text{Mn}^{2+}$  concentration is 0.07 mg/L, with an average high concentration of approximately 0.2 mg/L. The FCWTF was using  $\text{KMnO}_4$  for Mn oxidation and removal, but results were often unsatisfactory in terms of finished water Mn concentrations, particularly for low influent dissolved Mn levels. The utility had experienced colored water issues with treated water concentrations as low as 0.020 mg/L of total Mn, so the ultimate goal for Mn in finished water was set by FCWTF at 0.010 mg/L. The current operating target is less than 0.005 mg/L. The source of  $\text{Mn}^{2+}$  is the release of  $\text{Mn}^{2+}$  from the sediment through biological and chemical reduction in the lower depths of the reservoir. [Figure 7.33](#) illustrates the seasonal lowering of DO at the outlet from the reservoir to the FCWTF. [Figure 7.34](#) shows the total and dissolved Mn levels over the identical time period.

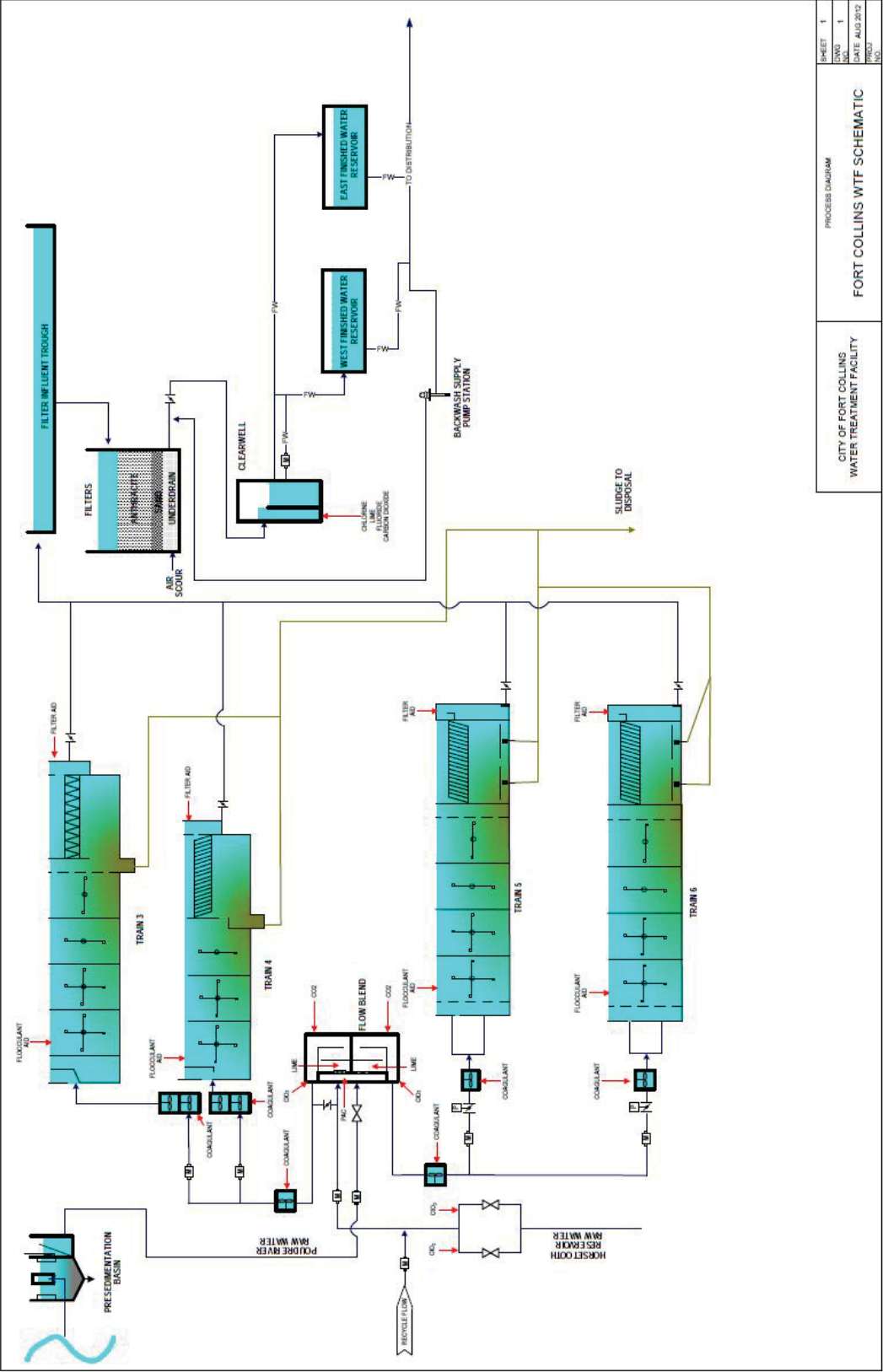
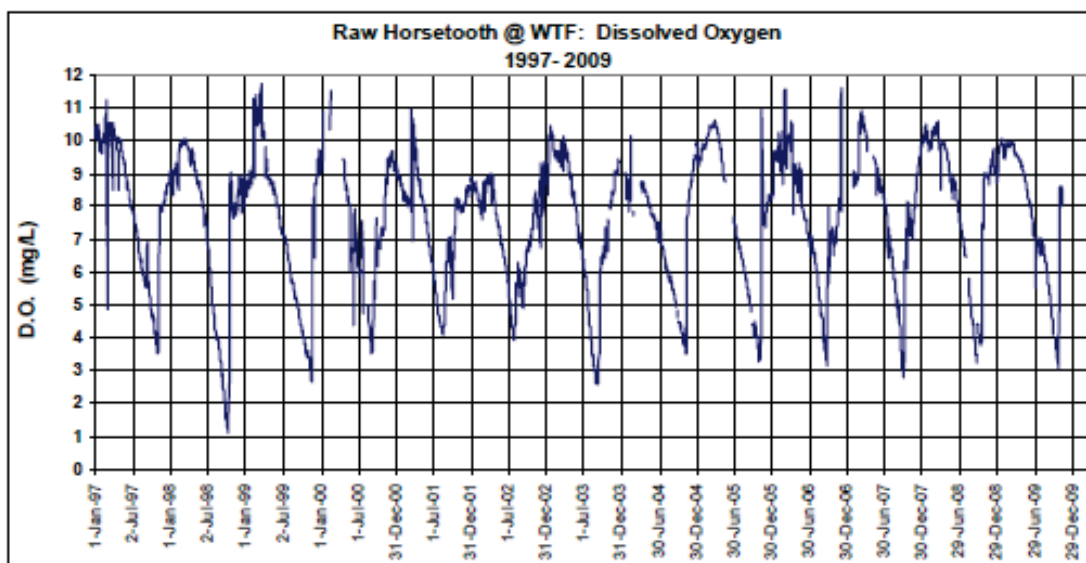
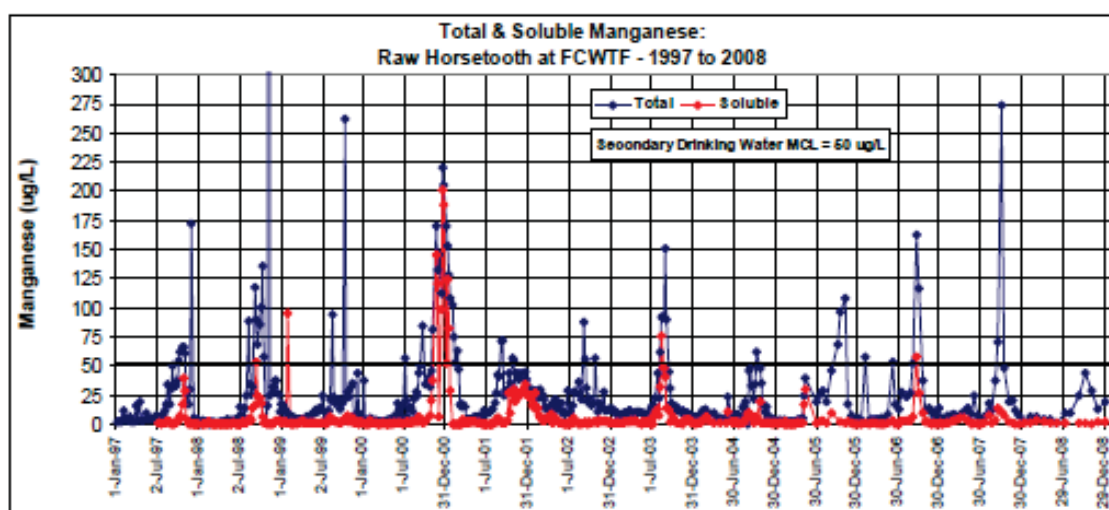


Figure 7.32 Schematic drawing of Fort Collins water treatment processes





**Figure 7.33 On-line dissolved oxygen measured at raw Horsetooth Reservoir at FCWTF sample station (Ref: City of Fort Collins Horsetooth Reservoir monitoring program)**



**Figure 7.34 Total and dissolved manganese measured at Raw Horsetooth Reservoir @ FCWTF sample station (Ref: City of Fort Collins Horsetooth Reservoir monitoring program)**

### *Evaluation of Oxidants*

Fort Collins undertook a study to evaluate chlorine dioxide ( $\text{ClO}_2$ ), potassium permanganate ( $\text{KMnO}_4$ ) and ozone ( $\text{O}_3$ ) for the oxidation of  $\text{Mn}^{2+}$  to  $< 0.005 \text{ mg/L}$ . Greensand filters were not included in the study. Instead this study was focused only on oxidizing  $\text{Mn}^{2+}$  prior to coagulation for removal in the sedimentation and filtration processes in the plant.

The study utilized raw water from Horsetooth Reservoir with characteristics listed in [Table 7.3](#). Concentrations of  $\text{Mn}^{2+}$  for experiments were adjusted to 0.060, 0.200 and 1.00 mg/L. Details of the experimental approach, methods and results can be found in Gregory and Carlson, 2003.

**Table 7.3**  
**Water quality characteristics of Horsetooth Reservoir**

Constituent	Range
pH	7.0 - 7.1
Temperature ( $^{\circ}\text{C}$ )	9 - 10
Alkalinity (mg/L as $\text{CaCO}_3$ )	25 - 30
Total organic carbon (mg/L)	3.4 - 3.6
SUVA (L/mg-min)	1.7
Dissolved oxygen (mg/L)	1.8 - 2.1
Ambient $\text{Mn}^{2+}$ (mg/L)	0.010 - 0.030
Turbidity (NTU)	3.5 - 4.5

Chlorine dioxide. The study results showed that  $\text{ClO}_2$ , at an appropriate dose, oxidized all three levels of  $\text{Mn}^{2+}$  within the available plant contact time (300 seconds). The oxidation rates at different concentration of  $\text{Mn}^{2+}$  were all rapid, but increased with initial  $\text{Mn}^{2+}$  concentration.

Potassium permanganate. Oxidation of  $\text{Mn}^{2+}$  by  $\text{KMnO}_4$  was shown to be much slower for initial  $\text{Mn}^{2+} = 0.06$  mg/L, taking 1,800 seconds for complete oxidation. At the highest initial  $\text{Mn}^{2+} = 1.0$  mg/L, the oxidation rate and final  $\text{Mn}^{2+}$  residual were comparable to the  $\text{ClO}_2$  results.

Ozone. Experimental results showed that the reaction time for  $\text{Mn}^{2+}$  oxidation using  $\text{O}_3$  was very rapid, being complete in less than 60 seconds. However, reaching a  $\text{Mn}^{2+}$  residual less than 0.01 mg/L only occurred when the initial  $\text{Mn}^{2+}$  concentration was 1.0 mg/L. When  $\text{O}_3$  doses were increased above the optimum, the residual dissolved Mn was always greater than 0.02 mg/L. This result appeared to be due to having oxidized Mn(II) beyond the desired Mn(IV) state to the dissolved state Mn(VII), forming  $\text{MnO}_4^-$ . Targeting the optimum dose requires overcoming the demand of naturally occurring organic matter without overdosing, creating a very narrow and shifting (as TOC changes) window for optimum operations. As a result, the distinctive pink color of  $\text{MnO}_4^-$  was observed in many of the  $\text{O}_3$  experiments.

Comparison of Oxidants. Comparing the results of the three oxidants tested,  $\text{ClO}_2$  was the most effective oxidant for reducing dissolved Mn residuals to  $< 0.01$  mg/L. Significant differences in reaction time between the three oxidants are evident from the results as shown in [Figure 7.35](#). Within the short period of time available in the FCWTF,  $\text{ClO}_2$  met the target  $\text{Mn}^{2+}$  residual for all concentrations of initial  $\text{Mn}^{2+}$ .

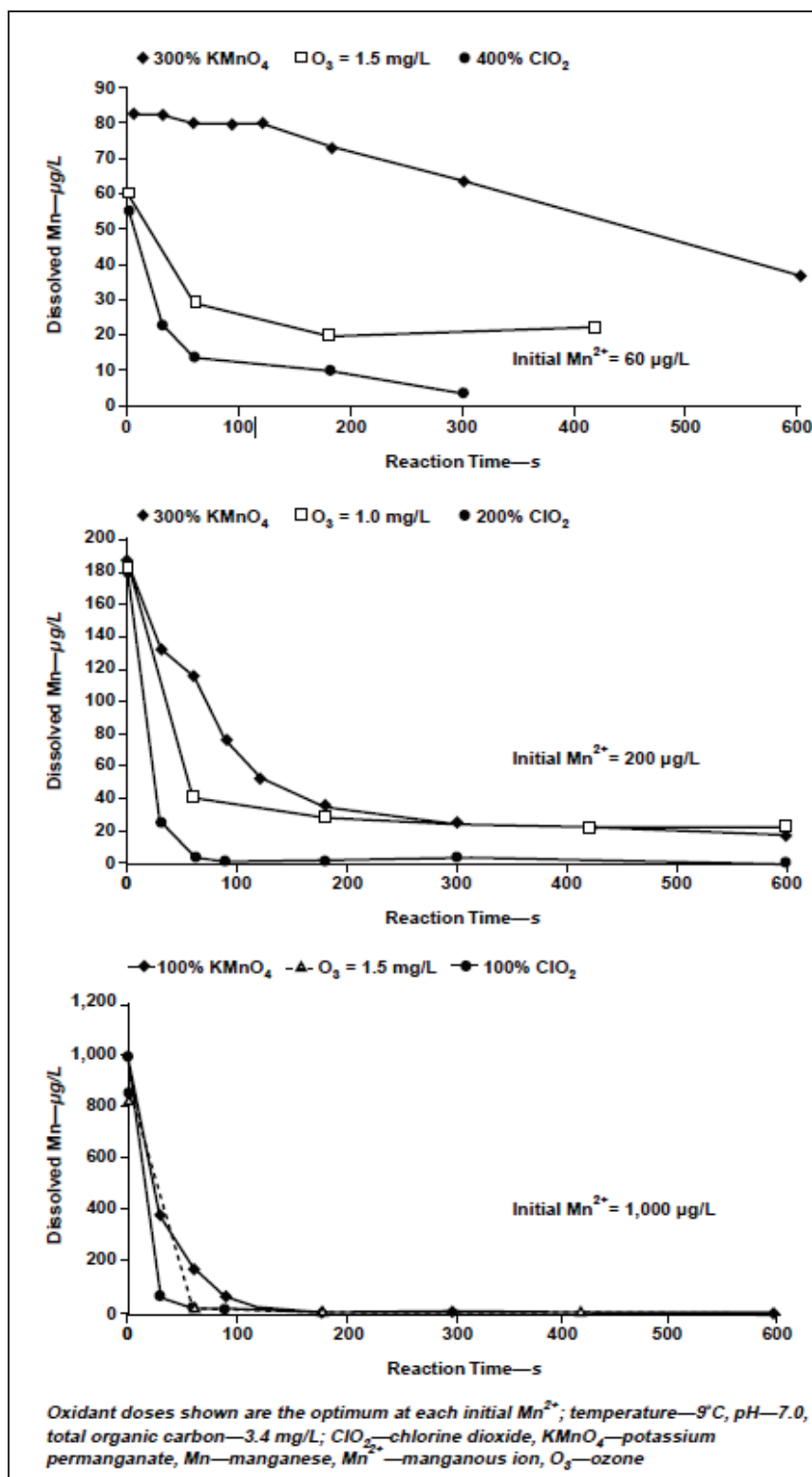


Figure 7.35 Bench-scale comparison of oxidation of Mn<sup>2+</sup> by KMnO<sub>4</sub>, ClO<sub>2</sub> and O<sub>3</sub> at three initial Mn<sup>2+</sup> concentrations. (Gregory, D. and K. Carlson 2003. Reprinted from *Journal AWWA* by permission. Copyright ©2003 by the American Water Works Association)

### ***Practical Application***

Based on the experimental results, FCWTF elected to use  $\text{ClO}_2$  for  $\text{Mn}^{2+}$  oxidation because the reactions were shown to be faster in Horsetooth water and  $\text{ClO}_2$  did not appear to be likely to create undesirable dissolved species. When needed,  $\text{ClO}_2$  is injected at the Horsetooth Reservoir raw water intake with doses ranging from 0.44 mg/L to 1.5 mg/L. At typical raw water  $\text{Mn}^{2+}$  levels between 0.07 and 0.2 mg/L, this treatment approach oxidizes to particulate form almost all manganese so that it is removed in settling and filtration.

During the early 2002 timeframe, work was done on the reservoir dam structures and the reservoir was drained to a very low level. Since that time, the Mn in the reservoir water has been very low, with no need to treat Mn.

**APPENDIX A. SAMPLE SPECIFICATION FOR FERRIC COAGULANT****SECTION I.**

**Ferric Sulfate 60%**, product must conform to ANSI/AWWA B406-06, Standard for Ferric Sulfate) and “NSF 60” certified.

The liquid ferric sulfate shall be manufactured from a Virgin Iron Ore (i.e. Hematite, Magnetite). The liquid ferric sulfate SHALL NOT be a by-product of any other process or be manufactured using materials that are either by-products or waste products from another process. The liquid ferric sulfate supplied shall contain no substances in quantities capable of producing deleterious or injurious effects on the health of those consuming water that has been properly treated with liquid ferric sulfate. The liquid ferric sulfate shall not contain specific impurities in excess of the following limits based on a liquid weight basis of ferric sulfate:

**SPECIFICATION**

Soluble Ferric Iron (Fe+++)	12% (+/- 0.10%)
Soluble Ferrous Iron (Fe++)	<0.2%
Water Insolubles	<0.1%
Specific Gravity (@ 60°F)	1.580

**IMPURITIES (+/- 10%)**

Arsenic	50mg/kg
Chromium	20mg/kg
Cadmium	5mg/kg
Lead	25mg/kg
Mercury	<2mg/kg
Silver	<2mg/kg
Titanium	25mg/kg
Magnesium	20mg/kg
Manganese	70mg/kg

**PLEASE NOTE:** A product data sheet and sample of Ferric Sulfate Product will be requested and analyzed. The Manganese (Mn) content of the product will be considered (in addition to cost) when identifying the product Supplier. The BOPU is very sensitive to Mn content of the product used in the drinking water treatment process and will therefore monitor Mn levels of the product submitted. Our goal is to be fiscally responsible to our customers, however the hidden Mn impacts (additional treatment requirements) will be weighed when considering product for use in the treatment process.





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## ABBREVIATIONS

AAS	Atomic absorption spectroscopy
°C	degrees Celsius
DO	Dissolved Oxygen
EPA	U.S. Environmental Protection Agency
Fe	Iron
Fe(II)	Ferrous ion
Fe(III)	Ferric ion
GWUDI	Ground Water Under the Direct Influence of Surface Water
H <sup>+</sup>	Hydrogen ion
HAA5	Haloacetic acids (sum of five regulated acids)
HAV	Health Advisory Value (for drinking water)
HLR	Hydraulic Loading Rate
ICP-MS	Inductively coupled mass spectrometry
IQ	Intelligent Quotient
IRIS	Integrated Risk Information System
mg/day	milligram per day
mg/kg-day	milligram per kilogram per day
mg/L	milligram per liter
Mn	Manganese (elemental)
Mn(II)	Manganous ion
Mn <sup>2+</sup>	Managanous ion
Mn <sup>3+</sup>	Manganic ion
Mn(III)	Manganic ion
MSDS	Material Safety Data Sheet
OH <sup>-</sup>	Hydroxide ion
ORP	Oxidation reduction potential
ppb	parts per billion
pH	Negative logarithm of hydrogen activity
RfD	Reference Dose for Chronic Oral Exposure
Scfm	Standard cubic per minute
SMCL	Secondary Maximum Contaminant Level

TOC	Total organic carbon
TTHM	Total trihalomethane
µg/L	microgram per liter
USGS	U.S. Geological Survey
WHO	World Health Organization

**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA05**

## **REGION 3 LOS ALAMITOS**



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CORROSION REPORT

PROJECT: Corrosion Engineering Evaluation of a Bolted Steel Water Storage Tank

STRUCTURE: 32,500 Gallon Bolted Steel Water Storage Tank  
(Cherry Plant Backwash Tank)

OWNER: Golden State Water Company

LOCATION: Los Alamitos, California

INVESTIGATED BY: Andre Harper, Project Engineer

DATE: November 2019

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I. GENERAL INFORMATION

A. Construction and Maintenance Details

The structure is a bolted steel water storage tank located in Los Alamitos, California, and is designated as the Cherry Plant Backwash Tank. The tank is approximately 21.5 feet in diameter and 12 feet high. The contractor and date of construction are unknown.

B. Site Conditions

The tank is on an asphalt and gravel site enclosed by a block wall, wrought iron gate, and backside of a building. There is adequate room around the tank for vehicles and equipment. No difficulty is anticipated for Contractor mobilization, assuming use of normal portable air compressor and related equipment.

There are office buildings and public foot traffic in close proximity to the tank which could be adversely affected by dust and contamination associated with abrasive blast cleaning and painting operations. Accordingly, extreme caution must be exercised during all cleaning and painting operations.

C. Existing Coating and Paint Systems

1. No records for the exterior paint or interior coatings were made available to HAE for review. The field investigation indicates the coating and paint systems to be the following:

a. Exterior Surfaces - Exterior roof and shell surfaces appear to be painted with

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an epoxy/urethane paint system.

- b. Interior Surfaces appear to be coated with an epoxy coating system.

D. Cathodic Protection System

No cathodic protection system is currently installed in the tank. There is no indication of a subgrade system for the underside of the bottom of the tank.

E. Heavy Metal Analyses

No samples of interior coatings or exterior paint were removed for analyses for the presence of heavy metals, specifically lead, zinc, and chromium compounds, as it was not included in the scope of work.

F. Contract Information

Harper & Associates Engineering, Inc. was retained by Golden State Water Company to accomplish field investigation of the tank to observe interior surfaces and conditions, with photographs taken to record conditions. This report has been prepared with recommendations and cost estimates.

This Corrosion Report is prepared solely on the basis of noted field investigation. Conclusions and recommendations are strictly those determined by Consultant to be consistent with the best and most experienced practice within the corrosion engineering profession.

II. INVESTIGATION

A. Investigation of the interior surfaces were accomplished as follows:

1. Underside of the roof, shell surfaces, bottom plates, and appurtenances were inspected by traversing the entire perimeter of the tank, climbing the interior ladder, and systematically traversing all structural elements and the bottom plates.
2. Light was supplied via high intensity portable light and natural light from the roof hatch and roof vent.
3. Various chipping tools were employed to examine typical areas of defective coating and corrosion within reach.
4. Photographs were taken of typical and specific areas to illustrate condition of surfaces.

III. OBSERVATIONS

A. Based upon the above reported investigation, the following observations were noted:

1. Interior Surfaces
  - a. Underside of Roof and Structural Members



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- 1) The coating system on the underside of the roof and structural members is in generally good condition with isolated areas of coating damage. (Photo I-2)
- 2) Moderate corrosion is present along the edges of the roof panel channel connections. (Photo I-2)
- 3) The edge of the center support plate and the nuts and bolts securing the rafters to the center support plate are severely corroded with metal loss present. (Photos I-3 and I-4)
- 4) The roof vent structure and nuts and bolts securing the vent to the roof are severely corroded. (Photo I-5)
- 5) The gusset plates and nuts and bolts securing the rafters to the shell are severely corroded with heavy mil scale. (Photos I-6 and I-7)
- 6) The stand-off bracket, U-bolt, and nuts and bolts securing the overflow to the shell are severely corroded. (Photos I-8 and I-9)

b. Shell, Column, and Appurtenances

- 1) The coating system on the shell and column is in generally good condition but the channels and nuts and bolts securing the panels together exhibit moderate to severe corrosion. (Photos I-10 through I-23)
- 2) The nuts and bolts and channels securing the shell panels are severely corroded below the high waterline with random bolt heads essentially gone. (Photos I-13 through I-20)
- 3) The channels and nuts and bolts securing the rectangular manway and inlet nozzle to the shell are severely corroded. (Photo I-21)
- 4) The nuts and bolts securing the stainless steel ladder to the shell are severely corroded. (Photos I-23 and I-24)

c. Bottom and Appurtenances

- 1) The coating system on the bottom plates is in generally good condition. (Photos I-20, I-26, and I-27)
- 2) The nuts and bolts securing the bottom plates are severely corroded. (Photos I-25 and I-26)

2. Safety, Health, and Code Features

- a. The roof hatch is undersized.
- b. The guardrailing does not turn onto the roof.

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- c. The nuts and bolts securing the ladder being severely corroded are not in compliance with Cal/OSHA Regulations.

#### IV. CONCLUSIONS

A. Based on the above noted observations, the following conclusions are drawn:

1. Interior Surfaces

a. Underside of Roof and Structural Members

- 1) The coating system on the roof plates and structural members is in generally good condition. The age of the coating system is unknown but epoxy systems typically have a 20 to 25 year life expectancy.
- 2) Isolated areas of coating damage on the roof plates and center support plate likely occurred during the erection of the tank.
- 3) Severe corrosion of the nuts and bolts is typically due to not properly coating the nuts and bolts (which appear to be carbon steel). The nuts and bolts securing the rafters to the support plate being severely corroded are significantly reducing the strength, which could result in the rafters falling into the tank. The rafters are only on the support plate by approximately 2" which, if the bolts fail, increases the chance of a rafter falling.
- 4) Severe corrosion of the nuts and bolts securing the vent structure is typically due to not properly coating the nuts and bolts (which appear to be carbon steel) and the moist warm air exhausting through the vent, which creates a more corrosive environment in this localized area.
- 5) Severe corrosion of the gusset plates securing the rafters to the shell appears to be due to not properly coating the edge of the plates originally in the shop. As corrosion developed along the edges of the plates, it migrated behind the coating on the plates. The corrosion on the nuts and bolts does not appear to be as severe where it can be seen; however, corrosion at the threads could be significantly worse and could result in the rafters falling into the tank.
- 6) Severe corrosion of the overflow stand-off bracket, U-bolt, and nuts and bolts securing the overflow to the shell appears to be due to utilizing carbon steel hardware and not properly coating these items. The strength of the nuts and bolts and U-bolt have been significantly reduced. If the bracket fails, the shell could be damaged as a result of the overflow falling into the tank.

b. Shell and Appurtenances

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- 1) The coating system on the shell is stained below the high waterline but is otherwise in generally good condition.
- 2) The severely corroded nuts and bolts securing the shell panels and appurtenances appears to be due to utilizing an inferior grade of galvanized nuts and bolts and channel. Based on the amount of metal loss that is present at this time, it is very likely that leaks and/or a split will occur in the future. The time frame in which this will occur cannot be determined.
- 3) The severely corroded nuts and bolts securing the ladder to the shell is a safety concern. The stainless steel ladder being secured to the carbon steel shell panels with either inferior galvanized or carbon steel nuts and bolts is creating a dissimilar metal condition, where the nuts and bolts and shell will corrode at an increased rate.

c. Bottom and Appurtenances

- 1) The coating system on the bottom surfaces is in generally good condition; however, the channel sections and nuts and bolts securing the plates are severely corroded.
- 2) Severe corrosion of the channels and nuts and bolts securing the bottom plates is due to the reasons noted above in 1. b. 2).

2. Safety, Health, and Code Features

- a. The guardrail not turning onto the roof is not in compliance with Cal/OSHA Regulations.
- b. The existing roof hatch does not provide the minimum 30" head clearance required by Cal/OSHA.
- c. The existing interior ladder should not be used until the corroded nuts and bolts are replaced.

V. RECOMMENDATIONS

- A. Based on the above noted observations and conclusions, the following recommendations are offered:

1. Interior Surfaces

- a. Due to the amount of corrosion at the structural connections, roof and shell channels, nuts and bolts, and appurtenances, it is recommended to replace the tank. It is HAE's opinion that rehabilitating the tank would not be cost-effective due to dismantling, replacing all channels, gaskets, nuts and bolts, and touch-up coating existing damaged areas and new areas of damage that would occur in the dismantling and re-erection of the tank. In addition, as noted below, there are safety items that need to be accomplished to make the

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tank Cal/OSHA compliant and the existing interior coating and exterior paint typically have a 20 to 25 year life expectancy, so it is anticipated the tank will need to be recoated and painted within a maximum of ten years.

2. Safety, Health, and Code Features
  - a. Sections of guardrailings should be installed on the roof, if the tank is rehabilitated.
  - b. A 36" x 36" roof hatch should be installed on the tank, if the tank is rehabilitated.
  - c. The nuts and bolts for the ladder should be replaced, if the tank is rehabilitated. HAE recommends not utilizing a stainless steel ladder. If a stainless steel ladder is used, it should be properly isolated from the structure.

## VI. COST ESTIMATES

- A. Based on current and previous projects of similar scope, preliminary cost estimates for work as noted in RECOMMENDATIONS were calculated by using data from those projects.

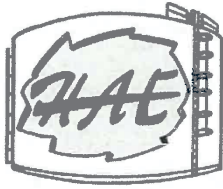
1. Interior Surfaces
  - a. Replacing the existing bolted tank with a new bolted tank with the same dimensions and utilizing the existing foundation would be in the cost range of \$60,000 to \$78,000.
2. Safety, Health, and Code Features
  - a. Installation of guardrailings sections would be in the cost range of \$3,500 to \$4,200.
  - b. Installation of a 36" x 36" roof hatch would be in the cost range of \$4,000 to \$4,800.
  - c. Replacing the nuts and bolts on the interior ladder with insulators would be in the cost range of \$1,500 to \$2,000.
3. No cost is projected for quality control inspection of work. An estimate would be furnished upon final determination of scope of work.

Respectfully submitted,

HARPER & ASSOCIATES ENGINEERING, INC.



Andre Harper  
Project Engineer



**HARPER & ASSOCIATES ENGINEERING, INC.**  
**CONSULTING ENGINEERS**

*1240 E. Ontario Ave., Ste. 102-312, Corona, CA 92881-8671  
Phone (951) 372-9196 Fax (951) 372-9198  
www.harpereng.com*

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**PHOTOGRAPHIC SURVEY**

**PROJECT:** Corrosion Engineering Evaluation of a Bolted Steel Water Storage Tank

**STRUCTURE:** Interior of the 32,500 Gallon Bolted Steel Water Storage Tank  
(Cherry Plant Backwash Tank)

**OWNER:** Golden State Water Company

**LOCATION:** Los Alamitos, California

**PHOTOGRAPHED BY:** Andre Harper, Project Engineer

**DATE:** November 2019

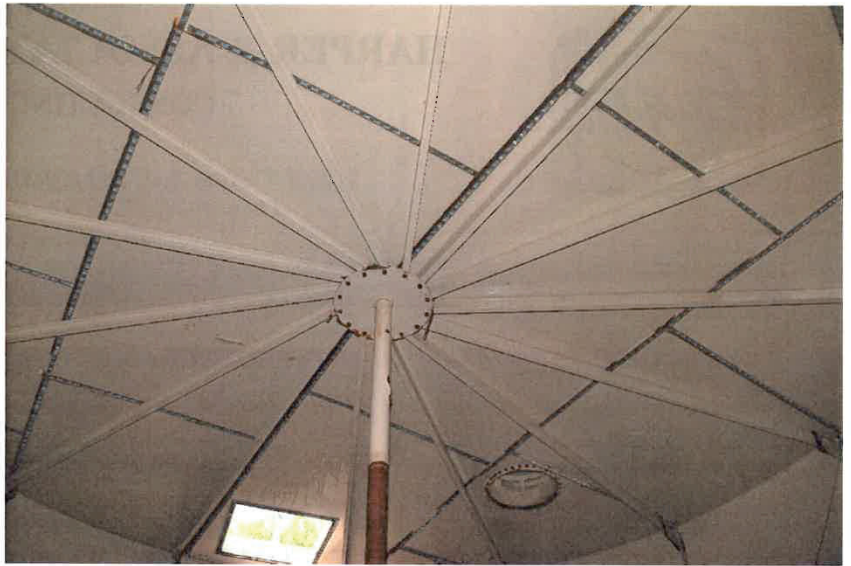
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I-1 View of the exterior of the Cherry Plant Backwash Tank, illustrating generally good condition of the paint system.

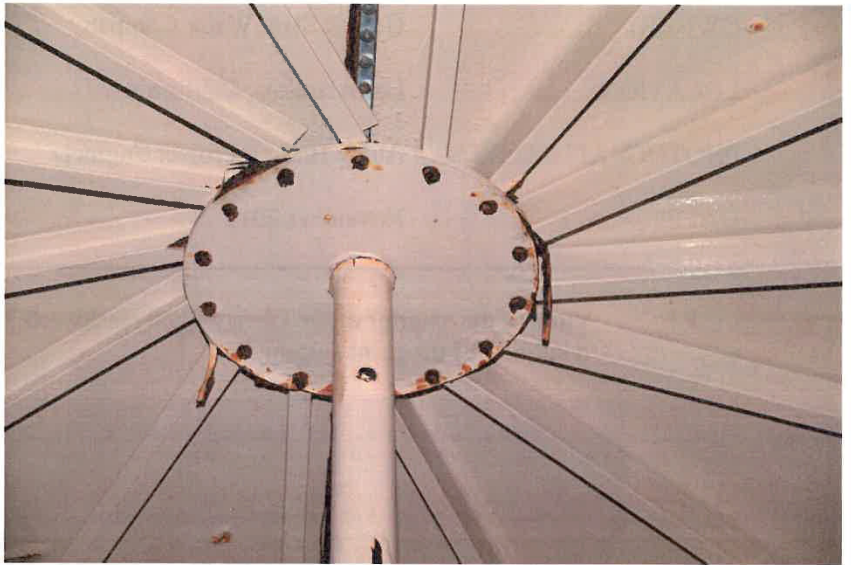




- I-2 View of the roof panels and galvanized channels, illustrating moderate corrosion along the edges of the channels and isolated areas of coating damage on the roof panels.



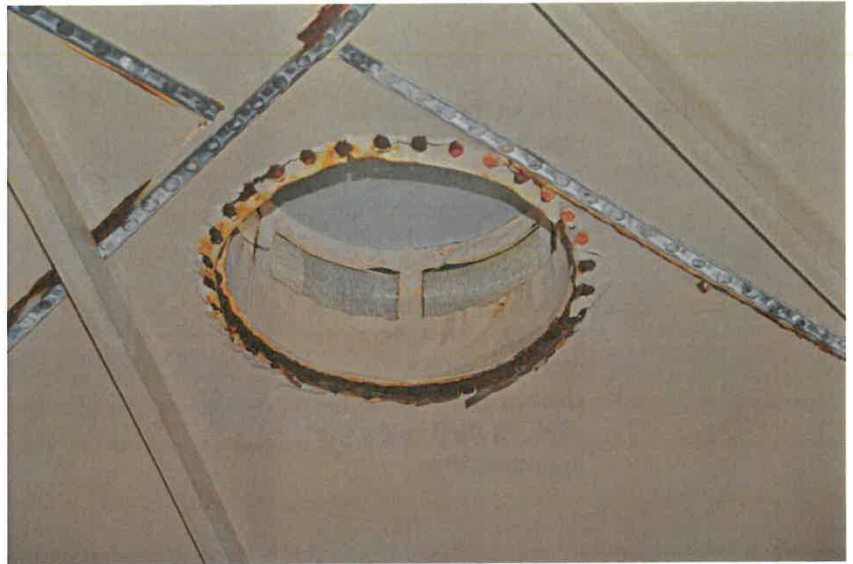
- I-3 View of the center support plate and adjacent rafters, illustrating severe corrosion on the edge of the support plate and the nuts and bolts securing the rafters to the support plate.



- I-4 Same as Photo I-3, except from a different angle. Note most of the nuts have almost completely corroded away.



- I-5 View of the roof vent, illustrating severe corrosion of the nuts and bolts securing the vent structure and at the screen openings.



- I-6 View of a rafter to shell connection, illustrating severe corrosion on the gusset plate and nuts and bolts securing the rafter to the gusset plate. Note vertical channel and bolts are in relatively good condition in this area.

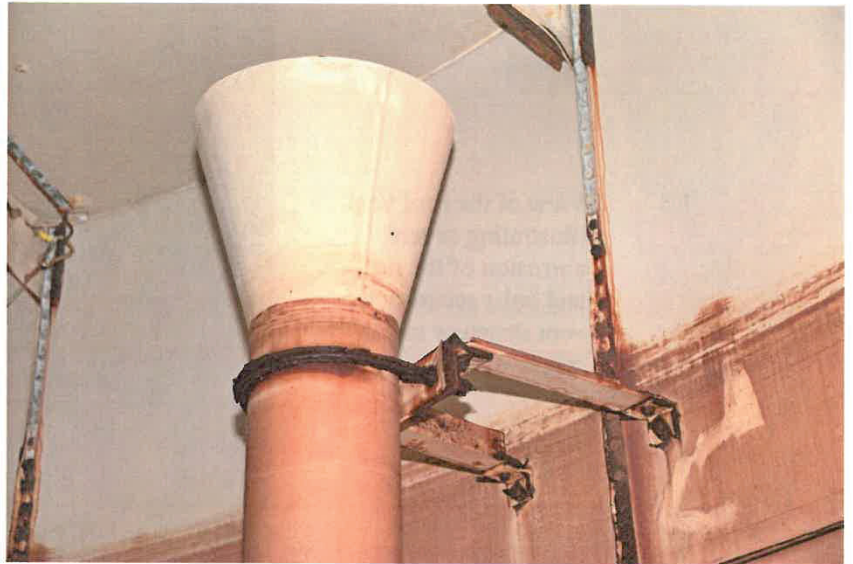


- I-7 Same as Photo I-6, except in a different location. Note delamination of the gusset plate with heavy rust scale on both sides of the plate.

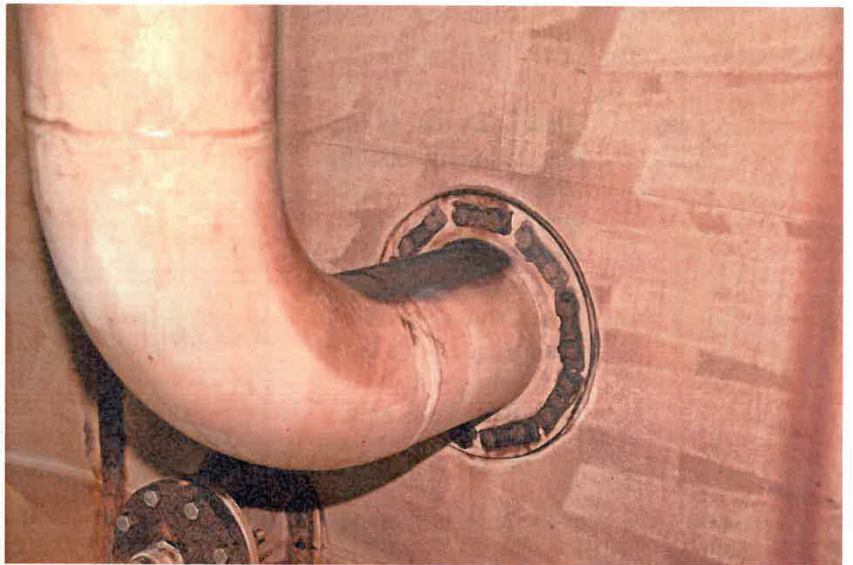




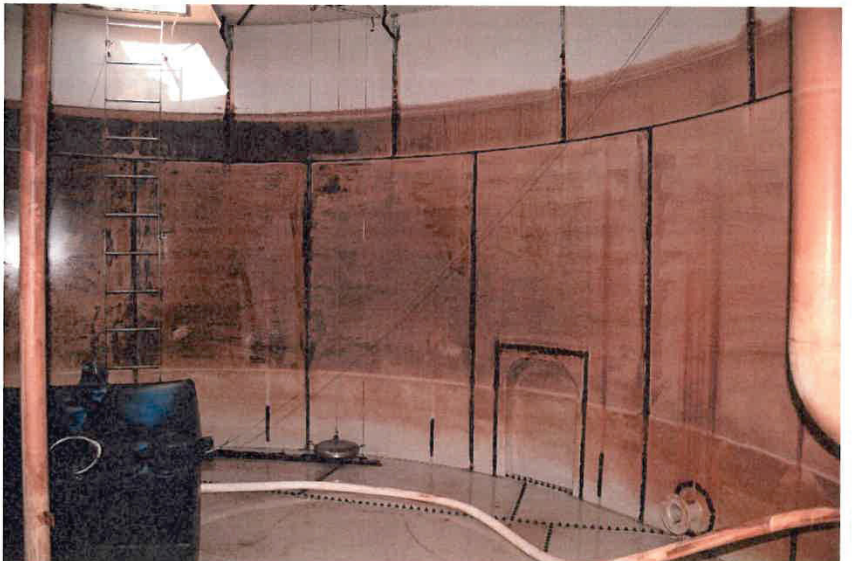
- I-8 View of the overflow pipe and stand-off bracket, illustrating severe corrosion of the U-bolt around the pipe and nuts and bolts securing the stand-off bracket. Note severe corrosion on the channel and bolts on the adjacent shell below the high waterline.



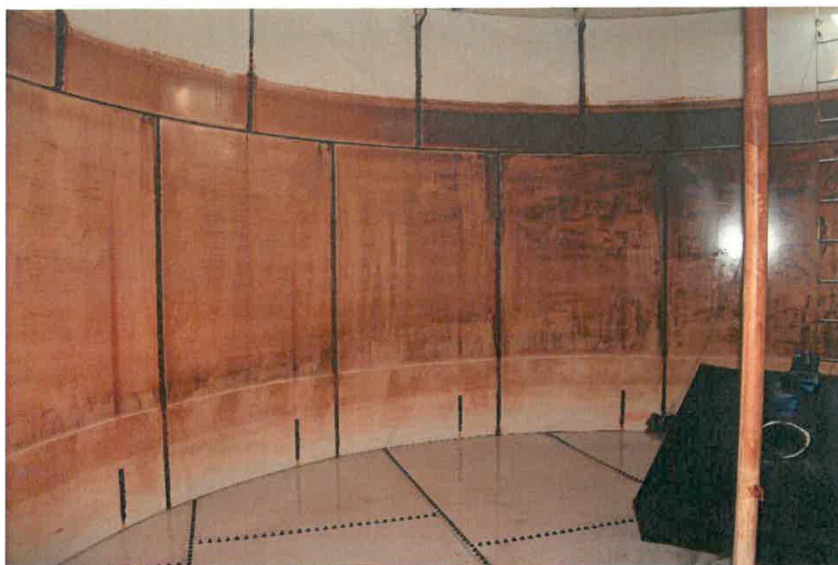
- I-9 View of the overflow pipe exiting the shell, illustrating severely corroded channels and nuts and bolts securing the overflow pipe to shell connection.



- I-10 View of a portion of the shell, illustrating severely corroded channel sections and nuts and bolts securing the shell plates below the high waterline. Note dark staining on the shell below the high waterline.



I-11 Same as Photo I-10,  
except a different  
portion of the shell.



I-12 Same as Photos I-10  
and I-11, except a  
different portion of the  
shell.



I-13 Close-up view of a  
channel section near the  
high waterline,  
illustrating severe  
corrosion of the channel  
and bolt heads in the  
water fluctuation zone  
and below.

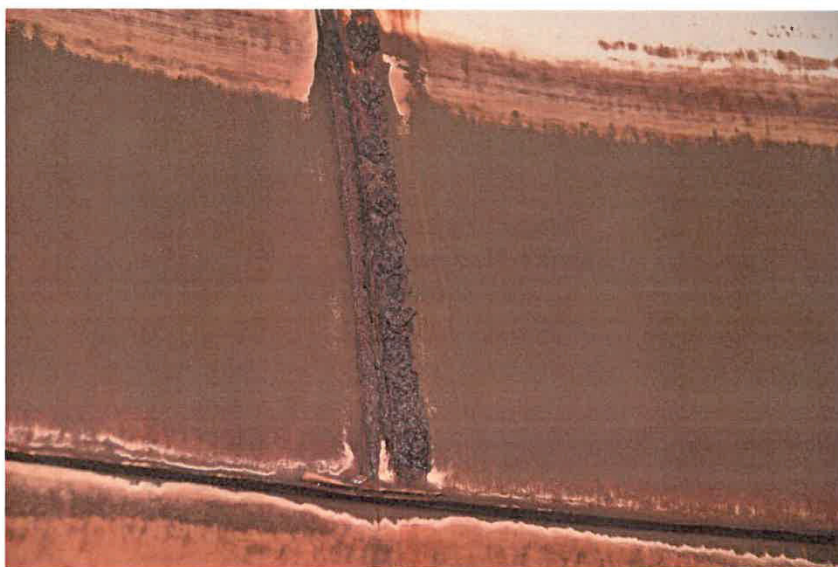




- I-14 Same as Photo I-13, except in a different location. Note 2 to 3 bolt heads just above the high waterline are essentially gone.



- I-15 Same as Photos I-13 and I-14, except in a different location.



- I-16 Same as Photos I-13 through I-15, except in a different location. Note one of the bolt heads just above the waterline is essentially gone.

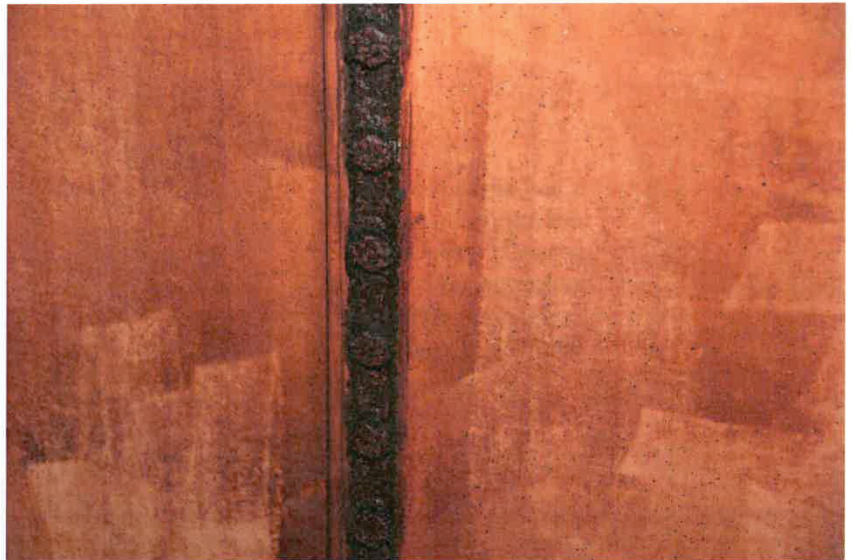




- I-17 Same as Photos I-13 through I-16, except in a different location.



- I-18 Same as Photos I-13 through I-17, except in a different location.



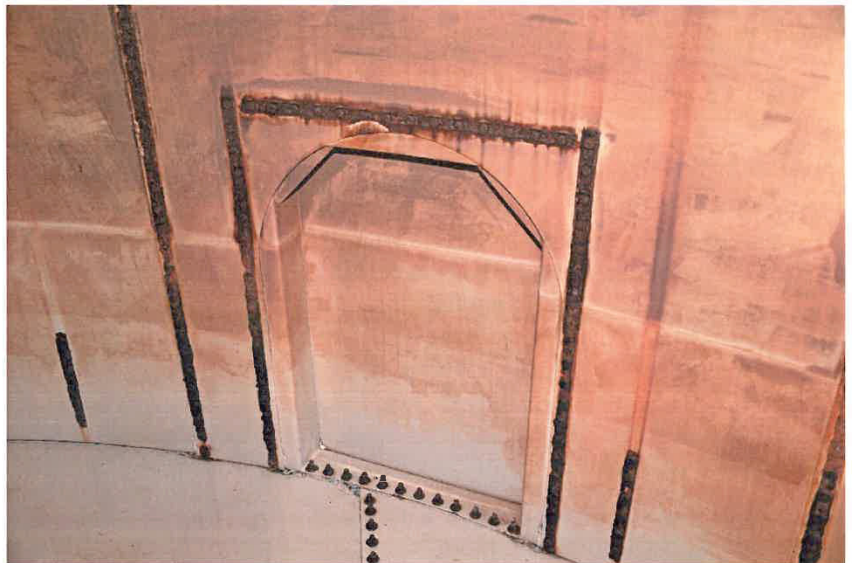
- I-19 Close-up view of a channel and bolt heads on the lower shell course, illustrating severely deteriorated channel and bolt heads. Note bolt head at the bottom of the photo is essentially gone.



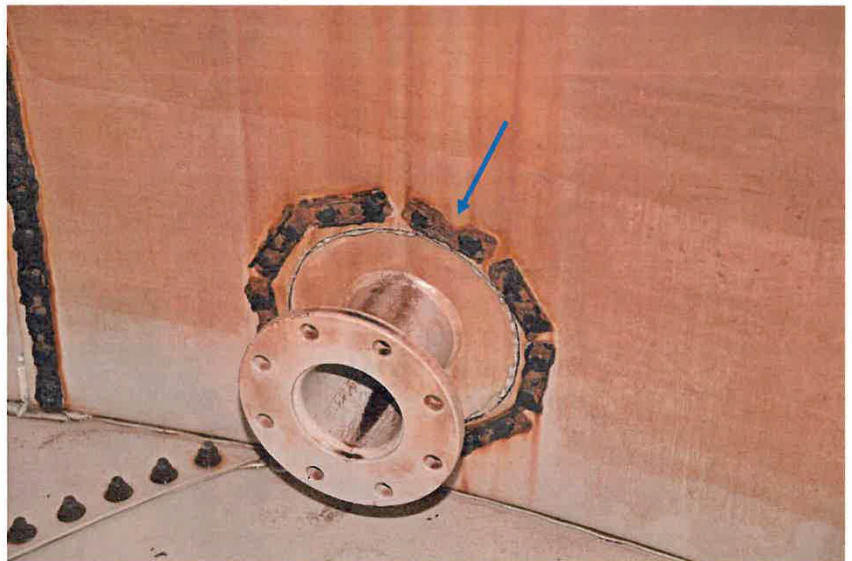
- I-20 View of the shell to bottom transition, illustrating severely corroded channel and bolts on the shell and severely corroded nuts and bolts securing the bottom plates.



- I-21 View of the rectangular manway, illustrating severely corroded channels and bolt heads at the perimeter of the manway.



- I-22 View of an inlet penetration, illustrating severely corroded channel sections and bolt heads securing the inlet nozzle. Note part of a channel section is missing due to severe corrosion.

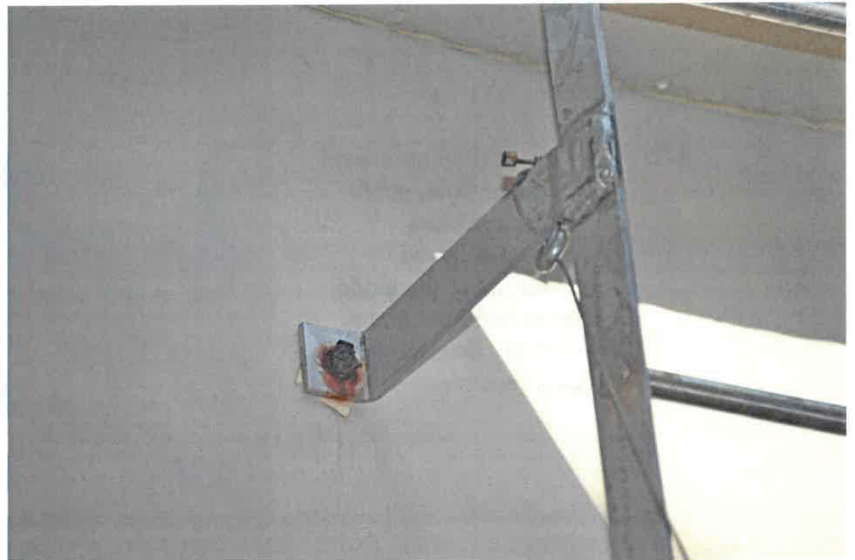




- I-23 View of the stainless steel ladder, illustrating good condition of the ladder and severe corrosion of the nut and bolt securing a stand-off bracket.



- I-24 Same as Photo I-23, except at a different stand-off bracket. Note the nut and bolt are severely corroded and almost gone.



- I-25 View of nuts and bolts securing the bottom plates, illustrating severely corroded nuts and bolts.



- I-26 Same as Photo I-25, except in a different location. Note nuts are essentially gone and the bolts are also severely corroded in this location.



- I-27 View of the liquid level indicator float, guide wires, and base, illustrating good condition of the guide wires and float and a severely deteriorated base (anchor).



**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT LA06**

**REGION 3**  
**LOS ALAMITOS**



## **PRELIMINARY DESIGN MEMORANDUM**

### **Florista, Site Grading & Paving Project West Orange County System Los Alamitos CSA Orange County District**

**Date:** January 31, 2020

**Project Location:** Florista Plant

#### **OBJECTIVE**

The objective of this project is to grade, pave and improve drainage at Florista plant.

#### **BACKGROUND**

The existing paving and grade does not drain surface water away from the steel reservoirs. Drainage ponds around and under reservoirs causing corrosion and increased maintenance.

#### **EXISTING FACILITIES**

The existing water infrastructure facilities:

- Three 1.5 MG welded steel reservoirs with a total capacity of 4.5 MG
- A water well with chlorination
- Two sets of water booster pumps

#### **PROPOSED FACILITIES**

The proposed improvements include:

- Remove paving and grade site
- Install electrical conduits
- Modify reservoir ring walls and drainage facilities
- Pave site with ACC

**See Project Cost Estimate for detail scopes.**

PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO

# **ATTACHMENT MV01**

**REGION 3**

**MORONGO VALLEY**

Sample Date	Site ID	sitelabel	Analyte	Result ug/L	Result pCi/L
1/5/2004 12:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	21	14.40
4/6/2004 12:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.60
7/6/2004 12:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	14	9.73
10/5/2004 12:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.90
11/14/2006 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	31	21.48
2/13/2007 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
5/15/2007 9:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
8/7/2007 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
11/6/2007 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
5/13/2008 8:35:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
8/12/2008 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
11/4/2008 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
2/3/2009 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
5/5/2009 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
8/4/2009 8:35:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
11/3/2009 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	19	13.17
2/1/2010 8:35:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
5/4/2010 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
8/3/2010 9:41:00 AM	MN-HI-W01	Highway Well	Uranium (total)	37	25.64
11/9/2010 8:25:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
1/25/2011 8:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	25	17.33
5/3/2011 11:05:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
8/2/2011 8:45:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
11/1/2011 11:05:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
9/25/2012 10:25:00 AM	MN-HI-W01	Highway Well	Uranium (total)	16	11.09
11/6/2012 8:40:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
2/5/2013 10:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
5/7/2013 9:20:00 AM	MN-HI-W01	Highway Well	Uranium (total)	19	13.17
8/6/2013 7:55:00 AM	MN-HI-W01	Highway Well	Uranium (total)	17	11.78
11/5/2013 9:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
2/11/2014 9:40:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
2/18/2014 8:45:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
5/6/2014 9:05:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
8/5/2014 9:30:00 AM	MN-HI-W01	Highway Well	Uranium (total)	21	14.55
11/18/2014 7:45:00 AM	MN-HI-W01	Highway Well	Uranium (total)	19	13.17
2/10/2015 10:14:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
5/26/2015 9:48:00 AM	MN-HI-W01	Highway Well	Uranium (total)	19	13.17
8/11/2015 10:00:00 AM	MN-HI-W01	Highway Well	Uranium (total)	19	13.17
11/10/2015 9:35:00 AM	MN-HI-W01	Highway Well	Uranium (total)	20	13.86
2/14/2017 9:37:00 AM	MN-HI-W01	Highway Well	Uranium (total)	26	18.02
8/1/2017 12:37:00 PM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
11/14/2017 8:53:00 AM	MN-HI-W01	Highway Well	Uranium (total)	24	16.63
2/6/2018 11:42:00 AM	MN-HI-W01	Highway Well	Uranium (total)	26	18.02
5/8/2018 10:25:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94

8/7/2018 10:26:00 AM	MN-HI-W01	Highway Well	Uranium (total)	25	17.33
11/6/2018 10:49:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
2/5/2019 9:57:00 AM	MN-HI-W01	Highway Well	Uranium (total)	22	15.25
5/14/2019 11:16:00 AM	MN-HI-W01	Highway Well	Uranium (total)	23	15.94
8/6/2019 12:00:00 AM	MN-HI-W02	Highway Well	Uranium (total)	25	17.33
11/5/2019 12:00:00 AM	MN-HI-W03	Highway Well	Uranium (total)	23	15.94

**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT P01**

**REGION 3  
PLACENTIA**





## Golden State Water Field Report

14-Nov-14

Underwater Cleaning / Inspection  
Clearview Round Tank

Potable Water Storage Tank

Submitted To:




Golden State Water  
Orange County District  
David Eikamp  
1920 West Corporate Way  
Anaheim, CA 92801  
Phone: 714-535-8010




Submitted By:



Potable Divers Inc.  
PO Box 474  
Vernal, UT 84078-0474  
  
Phone: (866) 789-3483  
Fax: (866) 913-4905  
E-mail david@potabledivers.com




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David Harvey Dive Supervisor




EXTERIOR ROOF									
<b>Concrete</b>									
Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Earth Covered	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Strength Members									
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>					
Seams/Joints	Fair								
Low Areas	Yes								
<b>Conclusion/Discrepancies:</b> The concrete roof exhibits stress cracks above the support columns In between the columns the roof has lower areas as the concrete is slightly sagging									
ACCESS HATCH									
Satisfactory		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>				
Construction	Galvanized steel								
<b>Coating</b>									
Corrosion	20%	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Proper Design		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>				
Locked		Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Gasket		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>				
Hinge	Fair								
Hatch Size	2 FT	X	18	In					
<b>Conclusion/Discrepancies</b> Access is a roof vent with corrosion on the edges and no screens or gaskets.									
VENTS									
Satisfactory		Y	<input checked="" type="checkbox"/>	N	<input checked="" type="checkbox"/>				
Construction	Galvanized								
<b>Coating</b>									
Corrosion	%	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Proper Design		Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Screens		Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Sealed Edges & Seams		Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>				
Cap/Cover		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>				
<b>Conclusion/Discrepancies</b> The side screens are in good condition and well sealed. The roof top vent has no screens in place and exhibits corrosion									

EXTERIOR SHELL				
Concrete				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Earth Embanked	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>Conclusion/Discrepancies:</p> <p>Exterior shell has a stucco type layer over the concrete and was found to be in excellent condition. No problematic concerns were noted</p> </div> <div style="width: 50%; text-align: center;">  </div> </div>				
EXTERIOR LADDER				
Construction Coated Steel				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Coating				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	No			
Pitting	No			
Delamination	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Welds/Joints	Good			
Supports	Good			
Safety Cage/Climb	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>Conclusion/Discrepancies</p> <p>Ladder and hardware were in excellent condition</p> </div> <div style="width: 50%; text-align: center;">  </div> </div>				
OVERFLOW STRUCTURE				
Coating Internal				
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Delamination	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Welds/Joints				
Supports				
Screens	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Attachments				
Foundation				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>Conclusion/Discrepancies</p> <p>Internal no exterior piping</p> </div> <div style="width: 50%; text-align: center;">  <p style="font-weight: bold; margin-top: 10px;">866-789-3483</p> </div> </div>				

FOUNDATION							
Concrete							
Satisfactory	Y	<input checked="" type="checkbox"/>				N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>				N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>				N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>				N	<input checked="" type="checkbox"/>
Erosion / Undermining	Y	<input type="checkbox"/>				N	<input checked="" type="checkbox"/>
Seismic Restraints		None					
Corrosion	Y	<input type="checkbox"/>				N	<input type="checkbox"/>
Tight	Y	<input type="checkbox"/>				N	<input type="checkbox"/>
<b>Conclusion/Discrepancies</b> Foundation was in good condition with no low areas sink holes or undermining noted.							
MANWAY ENTRIES							
Locations		None					
Coating							
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>			
Oxidized	Y	<input type="checkbox"/>	N	<input type="checkbox"/>			
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>			
Delamination	Y	<input type="checkbox"/>	N	<input type="checkbox"/>			
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>			
Welds/Joints							
<b>Conclusion/Discrepancies</b> No man way entries other than the roof vent on top of the tank							
<b>866-789-3483</b>							

INTERIOR ROOF				
Concrete				
Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Fair			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Vent Penetration	Poor corrosion present			
Roof Hatch	Poor corrosion present			
Conclusion/Discrepancies:	Roof exhibited stress cracks around the support columns and cracks extending away from the roof penetrations			
				
INTERIOR SHELL				
Concrete				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Wall to Roof Seam	Good			
Baffle/Support Walls	None			
Conclusion/Discrepancies:	Interior shell was found to be in excellent condition with no problematic concerns noted			
				
SUPPORT COLUMNS				
Construction Concrete				
Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Coating	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Welds	Fair			
Floor/Base Plates	Fair			
Conclusion/Discrepancies:	Cracks with efflorescence noted. Cracks are horizontal as well as vertical			
				




FLOOR													
Concrete													
Satisfactory	Fair	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	<input type="checkbox"/>								
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	<input type="checkbox"/>								
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	<input type="checkbox"/>								
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	<input type="checkbox"/>								
Strength Members				<input checked="" type="checkbox"/>									
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Seams/Joints	Good												
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	<input type="checkbox"/>								
Floor to Wall Seam	Good												
Conclusion/Discrepancies: Hair line cracks noted sporadically over the floor no efflorescence present no corrosion present Sediment depth on average was 1/8 of an inch													
MANWAY ENTRIES													
Coating None													
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>	 <p style="font-weight: bold; margin-top: 10px;">866-789-3483</p>							
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Seams/Welds													
Conclusion/Discrepancies: No other entries than the roof vent													
LADDER													
Construction No interior ladder													
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>	 <p style="font-weight: bold; margin-top: 10px;">866-789-3483</p>							
Coating													
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Seams/Welds													
Safety Cage/Climb	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	<input type="checkbox"/>								
Conclusion/Discrepancies: PDI provided a interior ladder for access													

APPURTENANCES									
<b>Influent</b>									
Construction		Mild Steel inlay							
<b>Coating</b>									
Satisfactory	Fair	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Corrosion	20% Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Seams/Welds		Fair							
Conclusion/Discrepancies:		Clear and unobstructed							
Corrosion noted on the interior									
<b>Effluent</b>									
Construction		Mild Steel with riser							
<b>Coating</b>									
Satisfactory	Fair	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Pitting	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Corrosion	80% Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Seams/Welds		Fair							
Conclusion/Discrepancies:		Extensive corrosion on the riser pipe clear and unobstructed							
<b>Telemetry</b>									
Construction		PVC							
<b>Coating</b>									
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>					
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>	X				
Seams/Welds		Good							
Conclusion/Discrepancies:		Pipe is in excellent condition							



OVERFLOW				
<b>Coating</b>				
Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Holidays	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	100%	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds	Poor			
Conclusion/Discrepancies: Overflow pipe is in critical condition with severe corrosion on pipe and funnel. The pipe has been repaired before and the repair is cracked and failing as well				



### Conclusion

Based on the results of this underwater inspection and the cleaning which took place, it appears this tank is in full operational condition and should continue to provide a reliable water storage capacity for potable water use with proper maintenance.

### Recommendations

PDI concurs with the recommendations of AWWA that all potable water reservoirs or storage tanks be cleaned and inspected at least every five years and in some cases, depending upon source waters, type and quantities of sediment, and presence (or lack thereof) of cathodic protection systems, more frequently.

The following recommendations are made to provide continued, uninterrupted service of your water storage tank:

- 1 Your tank should be inspected and cleaned every five years, as suggested by the AWWA. Routine inspections and cleanings provide ample time to perform remedial repairs to abnormalities discovered before having a chance to become problematic.
- 2 The roof vent used for a entry hatch is in poor condition. It has no gasket no screen and exhibits corrosion on all edges and openings. The vent needs to be replaced with a cap that will deflect the wind and elements and will allow for a screen and gasket.
- 3 The overflow pipe is severely corroded and needs to be replaced. The pipe has previous repairs that have cracked and are not holding up. With the amount of corrosion present it is a matter of time before the pipe leaks and the water will escapees through the corrosion.
- 4 The roof has stress cracks present at each of the support columns. The support columns also exhibit cracks horizontal and vertical. The roof needs to be evaluated by a structural engineer for integrity.

Goldenstate  
Clearview Round

# Potable Divers INC. Exterior Inspection Report

Nov 14 2014

AMERICAN WATER WORKS ASSOCIATION ANSI/AWWA D 101-53 (R86)						
EXTERIOR ROOF						
Safety Rail	Satisfactory	<u>X</u>	Coating	<u>Good</u>	Welds	<u>Good</u>
Access Hatch	Satisfactory	<u>NO</u>	Proper Design	<u>NO</u>	Locked	<u>YES</u>
External Coating	Satisfactory	<u>NO</u>	Oxidized	<u>NO</u>	Pitting	<u>NO</u>
Roof/Roof Panels	Satisfactory	<u>Stress cracks</u>	Low Areas	<u>YES</u>	Holes	<u>NO</u>
Vents	Satisfactory	<u>NO</u>	Proper Design	<u>NO</u>	Screens	<u>NO</u>
Cathodic Protection Plates	Satisfactory	<u>NO</u>	Sealed	<u>NO</u>	Secured	<u>NO</u>
EXTERIOR WALL						
Wall to Roof Seam	Satisfactory	<u>X</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
Wall Surface	Satisfactory	<u>X</u>	Cracking	<u>NO</u>	Spalling	<u>NO</u>
External Coating	Satisfactory	<u>X</u>	Oxidized	<u>NO</u>	Pitting	<u>NO</u>
No. 1 Ring (Bottom)	Satisfactory	<u>X</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
No. 2 Ring	Satisfactory	<u>NO</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
No. 3 Ring	Satisfactory	<u>NO</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
No. 4 Ring	Satisfactory	<u>NO</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
No. 5 Ring	Satisfactory	<u>NO</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
Ring(s)	Satisfactory	<u>NO</u>	Pitting	<u>NO</u>	Holes	<u>NO</u>
Access Ladder	Satisfactory	<u>X</u>	Bolts & Rungs	<u>Good</u>	Rust	<u>NO</u>
Overflow Structure	Satisfactory	<u>Internal</u>	Attachments	<u>NO</u>	Screen	<u>NO</u>
FOOTINGS/FOUNDATION						
Concrete Slab/Ring	Satisfactory	<u>X</u>	Cracking	<u>NO</u>	Spalling	<u>NO</u>
Overflow Structure	Satisfactory	<u>Internal</u>	Loose	<u>NO</u>	Rust	<u>NO</u>



Golden State  
Clearview Road

Potable Divers INC.

Nov 14 2014

AMERICAN WATER WORKS ASSOCIATION  
ANSI/AWWA D 101-53 (R86)

## ROOF

General Appearance	Excellent	Good	Fair	Poor	Critical
Interior Coating	N/A	Excellent	Good	Fair	Poor
Trusses	N/A	Excellent	Good	Fair	Poor
Roof Panels	Excellent	Good	Fair	Poor	Critical
Welds/Bolted Joints	Excellent	Good	Fair	Poor	Critical
Wall-to-Truss Gussets	N/A	Excellent	Good	Fair	Poor
Cracking	Absent	Slight	Extensive	Severe	Critical
Blistering	N/A	Absent	Slight	Extensive	Severe
Holidays	N/A	Absent	Slight	Extensive	Severe
Corrosion	N/A	Absent	Slight	Extensive	Severe
Vents & Screens	Intact	Fair	Damaged	Severe	Critical
Hatch	Poor				
Remarks/Discrepancies:					

## WALLS

General Appearance	Excellent	Good	Fair	Poor	Critical
Interior Coating	N/A	Excellent	Good	Fair	Poor
Welds/Bolted Joints	Excellent	Good	Fair	Poor	Critical
Walls/Wall Panels	Excellent	Good	Fair	Poor	Critical
Floor-to-Wall Joint/Weld	Excellent	Good	Fair	Poor	Critical
Cracking	Absent	Slight	Extensive	Severe	Critical
Blistering	N/A	Absent	Slight	Extensive	Severe
Holidays	N/A	Absent	Slight	Extensive	Severe
Corrosion	N/A	Absent	Slight	Extensive	Severe
Pitting	N/A	Absent	Slight	Extensive	Severe
Raffle/Support Walls	Absent	Slight	Extensive	Severe	Critical
Remarks/Discrepancies:					

## SUPPORT COLUMNS

General Appearance	Excellent	Good	Fair	Poor	Critical
Coating	N/A	Excellent	Good	Fair	Poor
Cracking	Absent	Slight	Extensive	Severe	Critical
Blistering	N/A	Absent	Slight	Extensive	Severe
Holidays	N/A	Absent	Slight	Extensive	Severe
Corrosion	N/A	Absent	Slight	Extensive	Severe
Pitting	N/A	Absent	Slight	Extensive	Severe
Floor Plates/Bases	Excellent	Good	Fair	Poor	Critical
Construction	Concrete	Steel	Wood		
Remarks/Discrepancies:					

## FLOOR

General Appearance	Excellent	Good	Fair	Poor	Critical
Interior Coating	N/A	Excellent	Good	Fair	Poor
Welds/Bolted Joints	N/A	Excellent	Good	Fair	Poor
Cracking	Absent	Slight	Extensive	Severe	Critical
Blistering	N/A	Absent	Slight	Extensive	Severe
Holidays	N/A	Absent	Slight	Extensive	Severe
Corrosion	N/A	Absent	Slight	Extensive	Severe
Pitting	N/A	Absent	Slight	Extensive	Severe
Remarks/Discrepancies:					

Interior Plumbing	Overflow	Severe	Water Level Sensors	Sediment depth	1/4"
	Influent	Poor	Cathodic Protection	N/A	Notes:
	Effluent	Poor	Ladder	N/A	
	Drain	Poor	Man Ways	N/A	

Critically  
Unsound



**PREPARED TESTIMONY ROBERT HANFORD and MARK INSCO**

# **ATTACHMENT P02**

**REGION 3  
PLACENTIA**



## Golden State Water Field Report

13-Feb-17

Underwater Cleaning / Inspection  
Clearview Square Tank

Potable Water Storage Tank

Submitted To:

Golden State Water  
Orange County District  
David Eikamp  
1920 West Corporate Way  
Anaheim, CA 92801  
Phone: 714-535-8010

Submitted By:

Potable Divers Inc.  
PO Box 474  
Vernal, UT 84078-0474

Phone: (866) 789-3483

Fax: (866) 913-4905

E-mail david@potabledivers.com

David Harvey Dive Supervisor

### EXTERIOR ROOF

#### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Earth Covered	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Low Areas	No			



Conclusion/Discrepancies: Steel plates cover the roof with sealed edges and seams.  
All flashing and hardware secured and in good condition

### ACCESS HATCH

Satisfactory Y ☐ N ☒

Construction Coated Aluminum

#### Coating

Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Proper Design	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Locked	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Gasket	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>

Hinge Good

Hatch Size 3 FT X 3 FT

Conclusion/Discrepancies Access hatch in excellent condition with gasket and lock in place



### VENTS

Satisfactory Y ☒ N ☐

Construction Galvanized

#### Coating

Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Proper Design	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Screens	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Sealed Edges & Seams	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cap/Cover	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>

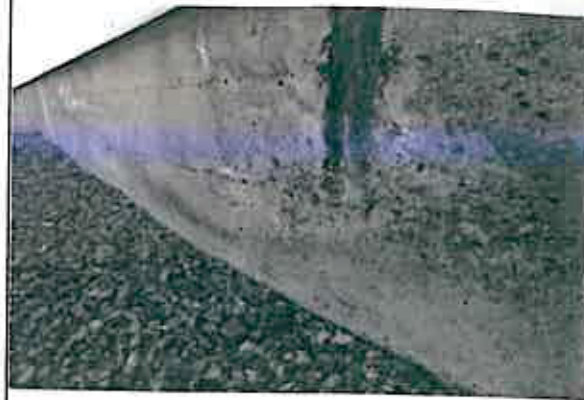
Conclusion/Discrepancies The side screens are in good condition and well sealed.



### EXTERIOR SHELL

#### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Earth Embanked	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>



Conclusion/Discrepancies: Exterior shell being mostly below grade is in good condition with no discrepancies noted

### EXTERIOR LADDER

#### Construction

#### Coated Steel

Satisfactory Y ☒ N ☐

#### Coating

Satisfactory Y ☒ N ☐

Oxidized No

Pitting No

Delamination Y ☐ N ☒

Corrosion % Y ☐ N ☒

Welds/Joints Good

Supports Good

Safety Cage/Climb Y ☐ N ☒

Conclusion/Discrepancies: Ladder and hardware were in excellent condition



### OVERFLOW STRUCTURE

#### Coating

Satisfactory Y ☒ N ☐

Oxidized Y ☐ N ☒

Pitting Y ☐ N ☒

Delamination Y ☐ N ☒

Corrosion % Y ☐ N ☒

Welds/Joints Good

Supports Good

Screens Y ☒ N ☐

Attachments Piped with screen

Foundation Concrete

Conclusion/Discrepancies: Pipe and fallout in good condition



## FOUNDATION

### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Erosion / Undermining	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seismic Restraints	None			
Corrosion	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Tight	Y	<input type="checkbox"/>	N	<input type="checkbox"/>

Conclusion/Discrepancies Foundation was in good condition with no low areas sink holes or undermining noted.



## MANWAY ENTRIES

Locations None

### Coating

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Delamination	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Welds/Joints				

Conclusion/Discrepancies

No man way entries other than the roof vent on top of the tank

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866-789-3483



### INTERIOR ROOF

#### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>

Vent Penetration Excellent

Roof Hatch Excellent

Conclusion/Discrepancies: Roof is constructed of overlapping steel plates. All seams and edges are sealed and in good condition. No corrosion or other problematic concerns



### INTERIOR SHELL

#### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Wall to Roof Seam	Good			

Baffle/Support Walls None

Conclusion/Discrepancies: Concrete is lined with a pvc liner. The top edges well secured with all hardware in place.



### SUPPORT COLUMNS

#### Construction None

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Honeycombing	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Coating	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds				

Floor/Base Plates

Conclusion/Discrepancies: Steel trusses support the roof there are no support columns



## FLOOR

### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Floor to Wall Seam	Good			



Conclusion/Discrepancies: Floor is covered with a pvc liner. Liner is in excellent condition  
with no discrepancies noted Sediment depth on average was <1/16"

## MANWAY ENTRIES

### Coating None

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds				

Conclusion/Discrepancies:  
No other entries than the roof vent



## LADDER

Construction	Aluminum			
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Coating				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Welds	Good			
Safety Cage/Climb	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>

Conclusion/Discrepancies: Ladder is in  
excellent condition



## APPURTENANCES

Influent equalization line

Construction Mild Steel inlay

Coating

Satisfactory	Fair	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	5% Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds	Good			

Conclusion/Discrepancies: Clear and unobstructed

Corrosion noted on the interior and outer edges of exterior



Effluent

Construction Slip lined steel

Coating

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Welds	Good			

Conclusion/Discrepancies: Effluent pipe is in excellent condition



Drain

Construction No dedicated drain line

Coating

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds				


Conclusion/Discrepancies:

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OVERFLOW				
<b>Coating</b>				
Satisfactory	Y	X	N	
Blistering	Y		N	X
Cracking	Y		N	X
Peeling	Y		N	X
Holidays	Y		N	X
Pitting	Y		N	X
Corrosion	Y		N	X
Seams/Welds	Good			
Conclusion/Discrepancies: Overflow funnel is in excellent condition with no discrepancies				



### Conclusion

Based on the results of this underwater inspection and the cleaning which took place, it appears this tank is in full operational condition and should continue to provide a reliable water storage capacity for potable water use with proper maintenance.

### Recommendations

PDI concurs with the recommendations of AWWA that all potable water reservoirs or storage tanks be cleaned and inspected at least every five years and in some cases, depending upon source waters, type and quantities of sediment, and presence (or lack thereof) of cathodic protection systems, more frequently.

The following recommendations are made to provide continued, uninterrupted service of your water storage tank:

- 1 Your tank should be inspected and cleaned every five years, as suggested by the AWWA. Routine inspections and cleanings provide ample time to perform remedial repairs to abnormalities discovered before having a chance to become problematic.
- 2 A small breach in the liner that was leaking water was noted during the inspection. The liner was repaired using aquata poxy A6 and NSF approved vulcanized rubber as a patch.
- 3 Several spots on the roof exhibited daylight. These areas need to be checked for proper sealing. Please review the photos and or video for location verification.  
Near the east wall in the center of the roof 5 spots of daylight (photo east wall center roof)  
North wall second I beam from the east wall along the wall seam (photo north wall 2nd I beam east wall)  
North west corner has 5 spots of daylight (photo Northwest corner)  
Large area of daylight in the center of the roof near the west wall (photo west wall center seam)





## Golden State Water Field Report

13-Feb-17

Underwater Cleaning / Inspection  
Clearview Round Tank

Potable Water Storage Tank

Submitted To:

Golden State Water  
Orange County District  
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1920 West Corporate Way  
Anaheim, CA 92801  
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David Harvey Dive Supervisor



### EXTERIOR ROOF

#### Concrete

Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Earth Covered	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Fair			
Low Areas	Yes			



Conclusion/Discrepancies: The concrete roof exhibits stress cracks above the support columns  
In between the columns the roof has lower areas as the concrete is slightly sagging  
Surface water collecting in the low areas

### ACCESS HATCH

Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>	
Construction	Galvanized steel				
Coating					
Corrosion	20%	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Proper Design		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Locked		Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Gasket		Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Hinge	none				
Hatch Size	2	FT	X	18	In



Conclusion/Discrepancies Access is a roof vent  
with corrosion on the edges and no screens or  
gaskets.

Spalling with crackin gnotted on the interior of the entry

### VENTS

Satisfactory	Y	X	N	X	
Construction	Galvanized				
Coating					
Corrosion	%	Y	X	N	
Proper Design		Y	X	N	
Screens		Y	X	N	
Sealed Edges & Seams		Y	X	N	
Cap/Cover		Y		N	X

Conclusion/Discrepancies The side screens are  
in good condition and well sealed. The roof top  
vent has no screens in place and exhibits  
corrosion



### EXTERIOR SHELL

#### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Earth Embanked	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>



Conclusion/Discrepancies: Exterior shell has a stucco type layer over the concrete and was found to be in excellent condition. No problematic concerns were noted

### EXTERIOR LADDER

Construction	Coated Steel			
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Coating				
Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	No			
Pitting	No			
Delamination	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Welds/Joints	Good			
Supports	Good			
Safety Cage/Climb	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>



Conclusion/Discrepancies: Ladder and hardware were in excellent condition

### OVERFLOW STRUCTURE

Coating	Internal			
Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Delamination	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Welds/Joints				
Supports				
Screens	Y	<input type="checkbox"/>	N	<input type="checkbox"/>

Attachments

Foundation

Conclusion/Discrepancies

Internal no exterior piping



866-789-3483

## FOUNDATION

### Concrete

Satisfactory	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Erosion / Undermining	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>

### Seismic Restraints

None

Corrosion	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Tight	Y	<input type="checkbox"/>	N	<input type="checkbox"/>

### Conclusion/Discrepancies

Foundation was in

good condition with no low areas sink holes or  
undermining noted.



## MANWAY ENTRIES

Locations None

### Coating

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Oxidized	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Delamination	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Welds/Joints				

### Conclusion/Discrepancies

No man way entries other than the roof vent on  
top of the tank

POTABLE DIVERS INC.



**866-789-3483**



### INTERIOR ROOF

#### Concrete

Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Seams/Joints	Fair			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>

Vent Penetration Poor corrosion present

Roof Hatch Poor corrosion present

Conclusion/Discrepancies: Roof exhibited stress cracks around the support columns and cracks extending away from the roof penetrations, rebar exposed from original construction



### INTERIOR SHELL

#### Concrete

Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Efflorescence Present	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Wall to Roof Seam	Minor spalling 5-6:00			

Baffle/Support Walls None

Conclusion/Discrepancies: Interior shell found to be in good-fair condition minor superficial cracks noted sporadically with efflorescence present.



### SUPPORT COLUMNS

#### Construction Concrete

Satisfactory	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Coating	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Welds	Fair			

Floor/Base Plates Fair

Conclusion/Discrepancies: Cracks with efflorescence noted. Cracks are horizontal as well as vertical, each column has cracking noted



## FLOOR

### Concrete

Satisfactory	Fair	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input checked="" type="checkbox"/>	N	<input type="checkbox"/>
Efflorescence Present	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Spalling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Scaling	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Exposed Aggregate	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Strength Members				
Exposed / Corrosion	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Seams/Joints	Good			
Honeycombing	Y	<input type="checkbox"/>	N	<input checked="" type="checkbox"/>
Floor to Wall Seam	Good			



Conclusion/Discrepancies: Hair line cracks noted sporadically over the floor  
no efflorescence present no corrosion present Sediment depth on average was <1/16"

## MANWAY ENTRIES

### Coating None

Satisfactory	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N	<input type="checkbox"/>
Seams/Welds				

Conclusion/Discrepancies:  
No other entries than the roof vent



## LADDER

Construction	No interior ladder		
Satisfactory	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Coating			
Satisfactory	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	N <input type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	N <input type="checkbox"/>
Seams/Welds			
Safety Cage/Climb	Y	<input type="checkbox"/>	N <input type="checkbox"/>

Conclusion/Discrepancies:  
PDI provided a interior ladder for access





## APPURTENANCES

### Influent

Construction Mild Steel inlay

#### Coating

Satisfactory	Fair	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Corrosion	20% Y	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Seams/Welds	Fair			

Conclusion/Discrepancies: Clear and unobstructed

Corrosion noted on the interior

### Effluent

Construction Mild Steel with riser

#### Coating

Satisfactory	Fair	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Pitting	Y	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Corrosion	80% Y	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Seams/Welds	Fair			

Conclusion/Discrepancies: Extensive corrosion on the riser pipe clear and unobstructed

### Telemetry

Construction PVC

#### Coating

Satisfactory	Y	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Blistering	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Cracking	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Peeling	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Holidays	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Pitting	Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Corrosion	% Y	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
Seams/Welds	Good			

Conclusion/Discrepancies: Pipe is in excellent condition



## OVERFLOW

### Coating

Satisfactory	Y		N	X
Blistering	Y		N	X
Cracking	Y	X	N	
Peeling	Y		N	X
Holidays	Y	X	N	
Pitting	Y	X	N	
Corrosion	100% Y	X	N	
Seams/Welds	Poor			



Conclusion/Discrepancies: Overflow pipe is in critical condition with severe corrosion on pipe

and funnel. The pipe has been repaired before and the repair is cracked and failing as well

## Conclusion

Based on the results of this underwater inspection and the cleaning which took place, it appears this tank is in full operational condition and should continue to provide a reliable water storage capacity for potable water use with proper maintenance.

## Recommendations

PDI concurs with the recommendations of AWWA that all potable water reservoirs or storage tanks be cleaned and inspected at least every five years and in some cases, depending upon source waters, type and quantities of sediment, and presence (or lack thereof) of cathodic protection systems, more frequently.

The following recommendations are made to provide continued, uninterrupted service of your water storage tank:

- 1 Your tank should be inspected and cleaned every five years, as suggested by the AWWA. Routine inspections and cleanings provide ample time to perform remedial repairs to abnormalities discovered before having a chance to become problematic.
- 2 The roof vent used for a entry hatch is in poor condition. It has no gasket no screen and exhibits corrosion on all edges and openings. The vent needs to be replaced with a cap that will deflect the wind and elements and will allow for a screen and gasket.
- 3 The overflow pipe is severely corroded and needs to be replaced. The pipe has previous repairs that have cracked and are not holding up. With the amount of corrosion present it is a matter of time before the pipe leaks and the water will escapees through the corrosion.
- 4 The roof has stress cracks present at each of the support columns. The support columns also exhibit cracks horizontal and vertical. The roof needs to be evaluated by a structural engineer for integrity.
- 5 The shell and the floor both exhibit cracks in the concrete. The cracks on the shell have efflorescence present. Most of the cracks are between 10 and 12 feet in length with several additional smaller cracks 3 feet long on the floor